All scientists were delighted to see Albert Fert and Peter Grünberg receive the 2007 Nobel Prize for Physics in Stockholm. This award has had a tremendous impact on policy makers, recalling every day of this turbulent year how a discovery made in a risky topic started 30 years ago has led to “a technology able to miniaturize hard disks useful for everyday life”.

There was a gap of 20 years between the breakthrough publications and the Nobel awards, a gap of ten years between the ideas originated then and the first reading-heads based on the discovery of GMR (giant magneto-resistance), and there have been a huge number of subsequent, now flourishing ideas thanks to convergence between the nanotechnologies and the rapidly growing field of spintronics.

It is that time scale of ten years that must be emphasized: a time, moreover, quite short compared to the usual delay between a scientific discovery and a marketable device, and yet a delay only reluctantly accepted by policy makers. It is just as crucial these days to recall the unique capability of the CNRS in having built a joint laboratory with the Thales (previously Thomson) company in only six months, more than 20 years ago. And the world-wide recognition of physicists working in CNRS laboratories cannot be explained if one denies the efficiency of the network based on these laboratories, with their orientation to excellence.

A consequence of the CNRS’s great strengths is that its laboratories – including the Néel Institute – are attractive to foreign physicists. Thus, Yuriy Bunkov came to Grenoble in 1992 from Moscow’s Kapitza Institute, and was appointed permanently as a Director of Research at the CNRS-Grenoble in 1995. It is a unique honor for each member of our laboratory to congratulate Yuriy Bunkov, who will receive the Fritz London Memorial Prize this August at the Low Temperature Physics Conference in Amsterdam.

This prestigious prize is to be awarded for the discovery of “spin superfluidity” and related phenomena. The phenomenon of spin superfluidity shows a current of spin (magnetization) behaving as an analogue of both superfluidity (a current of mass) and superconductivity (a current of electric charge). The Grenoble group has published some 25 articles on this subject. Among the 16 most cited papers, 10 come from Yuriy’s Grenoble period, some of them linked to the Grenoble-Moscow collaboration.

We are delighted to add three other names to the awards board for this year. Xavier Blase, who joined our laboratory recently after a scientific itinerary working with Steven Louie at Berkeley, with Roberto Car at EPFL and with J-Louis Barrat at Lyon, has won a Silver Medal of the CNRS for 2008 (see article inside). Bertrand Menaert has won a Crystal Medal of the CNRS for his exceptional creativity in the growth and machining of laser crystals, yielding two licensed CNRS patents. Bernard Barbara has been honored twice, as the recipient of the Grand Prix Alexandre Joannidès of the Académie des Sciences and the Gentner-Kastler Prize of the DPG and the SFP for 2007.

The next issue of the Néel Institute Highlights will give further scientific information relevant to these prizes in the context of our laboratory.

The present issue of Highlights features the observation of a new phenomenon in spintronics – a quantum phase transition in a molecular scale transistor – achieved by inserting a C_{60} molecule between two nano-machined electrodes, part of a nano-squid. Two electrons brought into this molecule form a singlet state (no magnetic moment) or a triplet state (with magnetic moment), depending on the electric field produced by a gate. The paper published in Nature (May 2008) increases the number of publications in Nature(s) and Science to 11 for this last year and a half.

Last but not least, we must emphasize the exceptional expertise of the technology “poles” and services of the Néel Institute, providing outstanding support to the Institute’s staff in meeting their experimental challenges and in their commitment to international collaboration/competition. In this issue, we present one such achievement, with transfer to industry. A total of about fifty of our EPC1-B preamplifiers, optimized for the measurement of very low voltage signals from high impedance sources, have been built in-house and are currently used throughout the Néel Institute. Their industrialization has now been launched by the Celian-CE3M company under license from the CNRS.

Grenoble June 29, 2008

Alain Fontaine

Director of the Néel Institute
The Department of Condensed Matter and Low Temperatures conducts fundamental studies of new states of matter (magnetism, charge density waves, superconductivity, etc.) and of the physics of helium between 100 μK and room temperature. The department develops transverse activities in cryogenic electro-technology, fluid mechanics, astronomy, the life sciences and associated applications (cryogenics, aero-space).

The Department of Nanosciences is engaged in the study of the physical properties of nanostructures: electronic transport, magnetism, nanomechanics, spectroscopy... at both experimental and theoretical levels. These nanostructures are prepared from various types of materials chosen for their specific properties - novel semiconductors, superconductors, metals, magnetic materials and molecules... Their fabrication at the nanometre scale - molecular films, nanowires, nanotubes, quantum wells and dots - leads to novel functions resulting from the most fundamental aspects of quantum physics.

The Department of Condensed Matter, Materials & Functions fosters fundamental research of materials and their applications. It has wide range experimental and theoretical expertises in material preparation, crystallography, electronic structure, magnetism, lasers, non-linear optics, catalysis and energy. The Department is distinguished by a strong interplay between physics and chemistry. It manages national projects at the ESRF and ILL and coordinates two thematic networks of the CNRS.
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Yuriy Bunkov, a CNRS researcher working at the Néel Institute, will share in the 2008 Fritz London Memorial Prize. This is considered the highest award in the field of low-temperature physics. Since its inauguration in 1957, nine of its winners have gone on to win the Nobel Prize.

Yuriy Bunkov, who joined the CNRS in 1998, conducts research on superfluid $^3$He at temperatures close to absolute zero, in order to learn more about the fundamental physics of matter and the cosmos.

The London prize will be awarded at the International Conference on Low Temperature Physics to be held in Amsterdam in August. Y. Bunkov shares the prize with Vladimir V. Dmitriev and Igor A. Fomin from the Kapitza Institute, Moscow, Russia. The prize will be given for “Phase Coherent Spin Precession and Spin Superfluidity of $^3$He-B”. The laureates have observed and identified a new coherent state of matter: a spontaneous, phase-coherent, macroscopic precession of magnetization. This is the phenomenon of spin superfluidity, the magnetic counterpart of the off-diagonal long-range order which is displayed by mass superfluidity in superfluids and by the superfluidity of electric charge in superconductors. This coherent state also represents a Bose-Einstein condensation (BEC) of spin-wave excitations or magnons. Historically, this was the first example of an experimentally stabilized Bose-Einstein condensate.

Since their discovery, the laureates have established many other consequences of this BEC state, such as the spin supercurrent, the spin-current Josephson effect, spin-current vortices, and non-topological solitons (called Q-balls in high energy physics). They also developed new measuring techniques based on coherent spin precession, which have made it possible to observe other novel effects in $^3$He superfluids. These observations include a vortex terminating on a soliton sheet, the Goldstone mode of the vortex with non-axisymmetric core in $^3$He-B, identification of the order parameter of $^3$He in an aerogel via a measurement of the $^3$He-B Leggett angle, and coherent precession in $^3$He-A, to name just a few.

At the Néel Institute, Yuriy Bunkov is now conducting experiments on superfluid $^3$He in three directions: studies of the deformation of the $^3$He order parameter in an anisotropic aerogel, experimental investigations of quantum fields using $^3$He as example (that is, modelling of elementary particle physics and cosmology) and development of a Dark Matter detector based on superfluid $^3$He at the lowest temperatures.

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The London prize, given once every three years, is named for Fritz London, a professor at Duke University who was the first to recognize the deep connection between superconductivity, superfluidity and the phenomenon of Bose-Einstein condensation. It was initially endowed by John Bardeen, who shared the Nobel Prize in 1972 for what is known as the BCS theory, which explained superconductivity.
In some materials, the charge density is not constant but acquires a spatial modulation below a transition temperature $T_c$. This phenomenon, known as the Peierls transition, is specific to quasi-1D materials. A similar phenomenon involving the spin density may also occur in low dimensional materials, yielding a spatial modulation of the spin density along the chains. In both cases, the modulation is described by its period, its amplitude and its phase.

In a real material, the modulation does not have a constant phase over the entire material, because defects and disorder introduce pinning centres which affect the amplitude and the phase of the modulation locally. Hence, the phase profile is the result of a compromise between the elastic energy that penalizes large phase gradients and the pinning energy that tends to fix the phase at the strongest pinning centres. These two ingredients produce metastable states as the result of collective pinning. Collective pinning is, however, frozen below 50 K via a glass-type order transition, as shown by dielectric susceptibility experiments. At very low temperature, the residual degrees of freedom in zero magnetic field are local defects in a strong-pinning model.

Larkin and Ovchinnikov have shown that a single strong-pinning impurity leads to a bound state made up of an electron-like soliton and a hole-like antisoliton. This results in a potential $V(\phi(y))$ with multiple minima, leading to slow relaxation, in agreement with the very low temperature heat relaxation observed in our experiments.

In equilibrium, the quasi one dimensional compound TMTTF$_2$Br has a spin-density ground state which is commensurate with the lattice period. When a sufficiently large magnetic field is applied, the heat relaxation experiments provide evidence that the ground state is no longer the same. The experiments are interpreted using the local model of strong pinning as the deconfinement of soliton-antisoliton pairs triggered by the Zeeman coupling to spin degrees of freedom. This results in a magnetic-field-induced density-wave glass for the spin carrying the phase configuration.

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Further reading:
One signature of strong electron correlation is a symmetry broken state, such as a charge or spin ordering, or superconductivity. In the phases that result from symmetry breaking, the basic electronic properties are profoundly modified.

The elasticity of broken symmetry ground states allows extra electrons to be accommodated by a local deformation of the ground state wavefunctions, whatever the method used to add electrons (doping, pumping or injection). Because of the ground state degeneracy, the local modifications can take the form of special, topologically nontrivial configurations, in particular solitons. Experimentally, the presence of solitons was identified in conducting polymers such as polyacetylene (2000 Nobel Prize in chemistry) where spin or charge carrying solitons appear under doping, optical pumping, and charge injection.

In layered electronic materials, perpendicular transport occurs by tunnelling between elementary conducting layers of nanometre thickness. Recently the method of "intrinsic coherent tunnelling", developed for High Tc superconductors, has been applied to layered materials having a Charge Density Wave (CDW) ground state.

Like the superconducting state, the CDW ground state corresponds to an electronic condensate opening a gap at the Fermi surface. However, the CDW condensate is spatially modulated and is coupled to a lattice distortion, thus forming an "electronic crystal" of overlapping singlet pairs of electrons.

Many charge density wave materials, such as NbSe$_3$, TaS$_3$, etc., are formed from elementary conducting chains assembled in conducting layers and separated by insulating layers, facilitating tunnelling spectroscopy. Investigations by this new technique have been advanced by development of sub-micron sized stacked structures, fabricated by means of focused ion beams, and of artificial single junction structures in NbSe$_3$.

Advanced interlayer tunnelling techniques having very high resolution provide real possibilities for probing amplitude and phase excitations of the uniform CDW ground state. Energies of both types of excitations lie inside the CDW gap energy $2\Delta$, and thus they can contribute to the interlayer tunnelling of the ungapped carriers. Conventional tunnelling techniques could not resolve these intragap states.

We reported recently the first direct observation of microscopic solitons in single electronic processes. In addition to the interband tunnelling across the gap $2\Delta$, an unexpected strong peak was seen at the intermediate voltage $2\Delta/3$ (Fig. 1); this peak is associated with the creation of microscopic solitons, as predicted. These solitons might correspond to the long sought special quasi particle: the spinon. Tunnelling can go through the soliton channel, solitons being more favourable quantum particles than electrons.

The phase solitons are associated with formation of dislocation lines in the CDW phase (CDW phase vortices). The energy of a single dislocation line is of the order of the Peierls transition temperature $kT_p$, that is about $0.1\Delta$. The phase solitons can be created by an electric field applied to the stacked junction [3]; their formation requires a threshold energy $eV_t \approx kT_p$ (Fig. 1). Particularly astonishing is the clear observation of a staircase structure in the tunnelling spectra due to entry of rows of charged dislocations – the aggregates of charged phase solitons above the threshold voltage $V_t$. Note the remarkable similarity between layered superconducting and CDW systems that manifests itself in similar mechanisms of phase decoupling via formation of phase vortices. In both cases a threshold energy for phase decoupling associated with $H_{c1}$ or $V_t$ is much smaller than the energy gap.

Further reading:

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The Néel Institute has a well established record of transferring its expertise in instrument technology to industry. The latest example is a preamplifier with exceptional specifications, the EPC1-B, that is optimized for very low voltage signals from high impedance sources such as those encountered in low temperature measurements. This instrument is now distributed by the company Celian-C3EM under licence from the CNRS.

The EPC1-B pre-amplifier was developed in-house for a variety of physical measurements (resistivity, specific heat, ...) requiring very high sensitivity, high precision and - in the case of low temperature measurements- high protection against perturbations. Compared to pre-existing preamplifiers, the noise level is reduced by a factor of 3. This translates, for example, into a reduction by a factor of 9 in the time required to do a measurement.

The EPC1-B is characterized principally by its low noise level, its high input impedance and its very accurate gain. A novel biasing circuit gives a very low cutoff frequency while maintaining excellent noise performance.

The general field of application is accurate measurements at high sensitivity. The EPC1-B is especially useful for amplifying signals coming from devices with high internal impedance such as piezoelectric sensors (accelerometers, microphones, pressure sensors ...) or capacitive sensors.

Before their industrialization, about 50 of these amplifiers were built internally and they are being used throughout the Néel institute.

Characteristics:
Gain values $10^2$, $10^3$, $10^4$ set manually or by TTL signals;
$f_{\text{min}} = 50$ mHz, $f_{\text{max}} = 13$ kHz;
$Z_{\text{in max}} = 300$ MOhms // 10 pF;
common mode rejection = 110dB from 1 Hz to 5 kHz.

Further information:
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Nanofluids are liquids that contain a small volume fraction of nanoparticles. These substances often exhibit unique properties without problems related to clogging and sedimentation. Here, the rheological properties of silica nanofluids are observed by passing them through microchannels.

The viscosity of nanofluids has been studied to a much lesser extent than their thermal conductivity. However, controlling the viscosity of liquid suspensions is important in diverse areas, ranging from preventing heart attacks to the design of miniaturized heat exchangers. The dynamic viscosity of nanofluids is not very well understood, especially the relative effects of the size of the nanoparticles and of the volume concentration. Compared to micrometer sized dispersed particles, nanofluids are subjected to colloidal interactions enhanced by Brownian motion, and to hydrodynamic interactions. The competition between these effects is characterized by the adimensional Peclet number $\text{Pe} \approx \frac{\eta_o \gamma d^3}{k_B T}$ where $\eta_o$, $\gamma$, and $d$ are the viscosity of the base fluid, the shear rate and the diameter of the particles respectively. For low $\text{Pe}$ values, the Brownian motion enhances the formation of aggregates of approximately 3 times the primary nanoparticle size. Hydrodynamic interactions become predominant for $\text{Pe} > 1$. However, reaching high $\text{Pe}$ values with nanosized particles is an experimental challenge because of the very strong shear rates that are necessary, and it is hardly attainable with conventional rheometers.

We have designed capillary microviscometers based on microchannels with integrated local pressure probes, to directly measure the hydrodynamics of monodisperse silicon dioxide nanofluids at the micrometer scale. The micrometer height of the channels allows us to reach strong shear rate values of about $2 \times 10^5 \text{ s}^{-1}$ while retaining laminar flow.

An anomalous enhancement of viscosity has been observed with increasing volume concentration (Fig. 2). The explanation is that the strong shearing forces in the microchannels affect the aspect ratio of the agglomerates. The effects of these interactions are more pronounced for large nanoparticles owing to higher $\text{Pe}$ values. The hydrodynamic interactions give way to the formation of trains of particles of reduced effective volume concentration. As a consequence, the relative viscosity is lowered. So, the aspect ratio of clusters may be thinned by a strong shearing motion. Very high shearing rates in microchannels appear to be a way for nanofluids to converge to a well-defined value of viscosity.

This work has been highlighted in Nature Nanotechnology as a landmark contribution of the year.

Fig. 1: Transmission Electron Microscopy image of an ensemble of SiO$_2$ particles. The circles 100 nm in diameter indicate the typical particle size.

Fig. 2: Evolution of the relative viscosity of SiO$_2$-ethanol nanofluids as a function of the volume concentration. The anomalous enhancement of the viscosity and the particle-size effect are a consequence of both aggregate size and hydrodynamic interactions. The viscosities lie well above the classical model of Einstein for microsized particles.

Further reading:
Domain walls in narrow strips of ferromagnetic materials have been proposed as carriers of information. The information could be transmitted either by external magnetic fields or by electric current pulses via the so-called spin torque effect. Information would be transported and processed as the domain walls propagate along a complex network of narrow magnetic strips.

Under given experimental conditions (temperature, magnetic field or current density values), the velocity of propagation of domain walls depends on both extrinsic parameters and intrinsic parameters. The extrinsic parameters are related to the geometry of the system (size, shape, roughness) and to structural defects, while the intrinsic parameters are related to material characteristics such as saturation magnetization, spin polarization of the conduction electrons and magnetic anisotropy or magnetization direction.

Better control of such parameters should allow optimization of domain wall velocities in view of using the walls as rapid and versatile carriers of information. For this purpose, we have chosen to develop model systems where one or several of the intrinsic or extrinsic parameters can be tuned independently.

We have recently demonstrated a method to tune the orientation of in-plane magnetic domains and domain walls in narrow ferromagnetic strips (cobalt) by manipulating an intrinsic system parameter, the magnetic anisotropy. This is achieved by inducing a uniaxial in-plane anisotropy in a controlled way, using oblique evaporation. A direct correlation between the imposed direction of magnetization and the domain wall orientation is found experimentally and confirmed by micromagnetic simulations. The domain walls in the strips are always found to be oriented along the oblique evaporation-induced easy axis, irrespective of the shape anisotropy.

The inclined orientation of the domain walls (see Figure) may be surprising, as it would seem more advantageous for the walls to be oriented perpendicular to the strip since this would minimize their length and thereby reduce the total exchange energy. However, the perpendicular orientation is not seen experimentally. Neither is it seen in the simulations. We thus attribute the inclination of the domain walls to magnetostatic effects: the compensation of the positive and negative magnetic volume changes $\rho = -\nabla M$ on either side of the Néel wall is obtained only if the domain wall is parallel to the magnetization direction in the domains. Thus, the static and probably also the dynamic properties of domain walls can be altered by controlling the wall orientation.

Extensive studies of domain wall propagation and dynamics are being done in the Néel Institute’s Micro and Nano-Magnetism group, in this and other model systems such as magnetic trilayers and epitaxial systems. Detailed information on the interaction between domain walls and spin-polarized currents will be obtained by high resolution static and dynamic imaging by XMCD-PEEM and by Kerr and MFM (Magnetic Force Microscopy).

![Figure 1: At top: X Ray Magnetic Circular Dichroism - Photoelectron Emission Microscopy image of inclined domain walls in narrow cobalt strips. At bottom: Simulated spin structure across an inclined domain wall, here of the Néel type where the spins rotate in the plane of the layer (the x-y plane).](image-url)
The operation of microelectronics circuits is described by the classical laws that prevail in the macroscopic world. These laws are profoundly changed for phenomena occurring at the atomic scale: the world of atoms and molecules is determined by quantum mechanics. Superconducting circuits provide a bridge between these two worlds. These electronics circuits are macroscopic in scale but they obey the laws of quantum mechanics. They constitute model systems for creating, analyzing and testing new properties in the domain of quantum nanoelectronics.

We have studied a circuit consisting of a Cooper pair transistor in parallel with a SQUID - a superconducting loop containing two Josephson junctions. The transistor is a small superconducting island connected to the external circuit by two Josephson junctions. Depending on the value of an applied grid voltage, this box can contain either zero or two electrons. The transistor can thus be switched between two different quantum states designated by $|\uparrow\rangle$ and $|\downarrow\rangle$ and constitutes a quantum bit, called a "charge qubit". The SQUID is a strongly non-linear resonator. This resonator can contain zero or one elementary excitations called plasmons, giving states designated by $|0\rangle$ and $|1\rangle$. It constitutes a second quantum bit, called a "phase qubit", which is controlled by an applied magnetic field and by the current flowing through the loop.

We have measured the transition probability between the coupled ground state $|0,\uparrow\rangle$ and the first two excited states $|1,\uparrow\rangle$ and $|0,\downarrow\rangle$, as a function of the frequency of a microwave field applied at the transistor grid or on the SQUID. These measurements provide the energy spectrum of the coupled circuit as a function of the external control parameters (grid voltage, magnetic flux through the SQUID). The frequency of the resonant transitions between the levels are of order 10 GHz and correspond to energies of about $10^{-23}$ J. The experiments are done in a dilution cryostat (T~ 30 mK) to avoid thermal population of the excited states.

When the energies of the two qubits are equal, their coupling lifts the degeneracy and produces anticrossings in the energy spectrum. States of maximum entanglement are then achieved. With our circuit, we have observed a controllable coupling between the two qubits. We have obtained a detailed description of the energy spectrum as well as the coupling using a quantum mechanical model. Thus, manipulation of entangled states and of quantum information is now possible in superconducting nanocircuits.

![Fig. 1: Scanning Electron Microscope image of (a) the transistor showing the superconducting island connected via two junctions to the SQUID and the grid for controlling its charge state and (b) the coupled circuit with SQUID at centre and transistor at left.](image1)

![Fig. 2: Energy spectrum of the coupled circuit as a function of grid voltage. The lifting of the degeneracy at $n_g=1/2$ reveals the coupling strength between the two qubits. Quantum theory without coupling (dotted traces) and with coupling (continuous curves).](image2)

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Further reading:
Graphene consists of a plane of carbon atoms arranged in a honeycomb structure. It is an unconventional two dimensional system with properties that appear more and more fascinating to researchers. The fact that it can be grown on silicon carbide substrates holds high promise for its future application in nano-electronics. However, it is essential to establish whether the remarkable properties of graphene are retained for a system of carbon planes in close proximity to a substrate. We have addressed this question by a combination of Scanning Tunnelling Microscopy (STM) measurements and ab-initio calculations of the electronic structure.

The key to the quite exceptional electronic properties of graphene lies in the symmetry of its crystal structure. The unit cell consists of two strictly equivalent carbon atoms, yielding a “new” degree of freedom compared with other 2D systems. The question is: does this symmetry remain intact for a graphene plane in contact with a silicon carbide surface or with another plane of graphene?

Since 2006, the Néel Institute has been applying its expertise in materials science to the growth of graphene on SiC substrates, starting from a method originated by W. de Heer and C. Berger’s team at Atlanta. By heating a hexagonal single crystal of SiC to around 1200°C in ultra-high vacuum, we can control very accurately the number of planes of graphene produced. For the case of a single plane (Fig. 1(a)), the STM image shows an equivalent contrast for all carbon sites, as expected for a graphene plane with no or very low interaction with its environment. Note that the image also shows a long distance modulation induced by the interface morphology.

The ab-initio calculations have allowed us to investigate the question of the interaction with the substrate. The calculations show that a buffer plane of carbon atoms is formed at the interface (indicated by the arrow in Fig. 1(b)), and that this decouples the planes of graphene from the substrate. The calculations also indicate that these planes are doped by charge transfer from the substrate. The doping effect is strongest for the planes closest to the substrate. This explains why, even when several graphene planes are present, the main contribution to electronic transport is made by a single plane, as suggested by magneto-transport measurements.

**Further Reading:**
A new way to make quantum dots - a slice in a wire

The growth of semiconductor nanowires is a rapidly developing field with potential for creating novel opto-electronic devices. We are interested in the nanowire geometry for two principal reasons: (i) Nanowires provide a new way to construct quantum dots, namely as a short slice inserted in a wire, with shape and density very well controlled as compared to the usual technique of “self-organized” epitaxial growth of quantum dots (ii) Nanowires can provide optimum light extraction, by acting as a wave-guide for photons emitted by an inserted quantum dot. This can provide a nano-emitter efficient enough to operate as a “single photon generator”, an essential component in quantum cryptography and quantum computation.

We have developed growth techniques for such structures using the large bandgap semiconductor systems GaN/AlN and CdSe/ZnSe, where there is hope that single photon sources can be made to operate at room temperature. The wires are grown by Molecular Beam Epitaxy either directly on the substrate for the nitride materials (Fig.1) or using a gold catalyst to initiate uni-dimensional growth for the selenides. For GaN, controlled columnar growth can be induced by an appropriate choice of the ratio between gallium and nitrogen fluxes. In contrast to the plastically relaxed two dimensional layers of GaN grown on mismatched substrates, GaN wires are essentially isolated objects, relaxed elastically with respect to the substrate, without any structural defects. Also, we can achieve one or several insertions of GaN between AlN barriers by switching the molecular fluxes (Fig.1, at right). Wires of this kind can be isolated for measuring optical properties of an individual GaN emitter.

An optical study for the case of a ZnSe nanowire containing a CdSe dot slice is shown in Fig. 2. With this nanostructure, we have demonstrated controlled generation of single photons at 220 K, a temperature accessible with Peltier cooling devices. This is the highest operating temperature recorded so far for a semiconductor quantum dot.

This work was done by the CNRS and CEA joint Grenoble group: “Nanophysique et Semiconducteurs”.

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Further reading:
• “Exciton and bi-exciton luminescence from single GaN/AlN quantum dots in nanowires”, J. Renard, R. Songmuang, C. Bougerol, B. Daudin, B. Gayral, Nanoletters (accepted May 2008).
Observation of a quantum phase transition in a molecular scale transistor

As physical objects become smaller, quantum effects become dominant and easier to measure. Thus, nanometer size quantum objects (in this work a C60 molecule) are propitious for observation of the new quantum phenomena associated with spin electronics. Such objects act as artificial atoms and can be controlled by external parameters such as magnetic field, electric potential or light. With its electrons confined at the nanometre scale, a quantum object’s charging energies can exceed a degree Kelvin, allowing study of quantum phenomena like Coulomb blockade and the Kondo effect over a large range of parameters at cryogenic temperatures.

When the wave function that describes a large number of particles obeying the laws of quantum mechanics can be changed continuously, a transition can be induced between two ground states with distinct symmetry. This is a purely quantum critical phenomenon which reveals new physics, as yet hardly explored. The quantum phase transition is fundamentally different from classical phase transitions like the liquid-gas transition or the appearance of ferromagnetism where thermal fluctuations play a major role. An external control parameter, for example a magnetic field or an electrostatic coupling, is needed to switch the system into a state where the disorder is induced by zero-point quantum fluctuations.

In reality, observations of this kind of phenomenon are always made at a low, non-zero temperature, so one can observe only the remanence of the zero temperature singular point. Studied usually in macroscopic size objects, the quantum phase transition can be achieved at the nanometre scale by combining the quantum states of a magnetic molecule with the electronic states in the connection circuit.

We have shown that a single-molecule quantum dot based on fullerene operates like a transistor with an even number of electrons. At very low temperature (35 mk), the magnetic triplet state conducts current well, thanks to a spin-assisted current enhancement called the Kondo effect. In contrast, the singlet state of the molecule is non-magnetic and so does not show this effect. The observation of these two states can be tuned electrostatically by the means of a local gate. On a more fundamental level, it is interesting how the Kondo effect disappears as the device is tuned from magnetic to non-magnetic. This change in the magnetic configuration of the device, induced by a non-thermal parameter, unveils a quantum phase transition in a nanoscale device. This kind of physics is of great current interest and, in addition, our experimental results offer new possibilities for controlling and manipulating the states in molecular spintronics.

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Further reading:
Xavier Blase, CNRS silver medalist

CNRS researcher Xavier Blase, who arrived at the Néel Institute in March 2008, has been awarded a CNRS silver medal for “Major contributions to the development of ab initio quantum simulations in France.”

Xavier Blase was recruited by the CNRS following his PhD with Steven Louie at University of California-Berkeley and a postdoc in Roberto Car’s team at the Ecole Polytechnique Fédérale de Lausanne. From 1996 until his recent move to the Néel Institute, he was based at the Laboratory for Condensed Matter Physics and Nanostructures (LPMCN, a joint laboratory of the CNRS and of Claude Bernard University, Lyon).

In his research work, Xavier Blase has explored varied fields of condensed matter physics, ranging from the growth mechanisms of nanotubes through the superconductivity properties of diamond and doped silicon to electronic transport in molecular systems. Involving both methods-development and applications, his research activity highlights the increasing role of ab initio quantum simulations for understanding physical phenomena in all areas of condensed matter science. His novel ideas allied to a clarity of exposition have been invaluable both to his theoretician colleagues - helping them to an understanding of extremely complex concepts - and to the many experimentalists he has worked with.

Xavier Blase learnt the science which became the basis of his subsequent career during his years at Berkeley and Lausanne. This was numerical simulation in solid state physics, and especially the application and the development of programmes for ab initio calculations based on the density function theory (DFT) and beyond (the GW approximation). Those years also coincided with an explosion of research in the nanosciences, a field where the combination of theory and experiment has proved particularly important. This is essentially because probing the “nanoworld” is a very difficult task: Often, the data signals that come out of the spectrometers and microscopes can be interpreted reliably only with the help of detailed calculations and simulations. In this respect, Blase’s skills in ab initio calculation techniques, together with his specialist knowledge of many aspects of solid state physics and nanostructures, brought him quickly to the forefront on the international scene. Especially, he became well known as a world expert in theoretical models for carbon and boron nitride nanotubes.

Xavier Blase’s subsequent career has been characterized by his attention to the needs of experimentalists. His availability, his open-mindedness and his dynamism are such that the foremost researchers in materials studies have called on him, leading to numerous collaborations both on nanostructured materials (nanotubes, nanowires,...) and on macroscopic materials (clathrates, diamond, doped silicon...).

Xavier Blase is also convinced that scientific knowledge should be shared as widely as possible. He attaches considerable importance to communicating his results to non-scientists and has reflected extensively on the economic, social and ethical consequences of scientific research. The CNRS’s decision to award him a silver medal is a particularly gratifying and judicious choice.

Text by Jean-Christophe Charlier
Professor at University of Louvain

The CNRS Silver Medal:
The CNRS awards a limited number of silver medals each year in all fields of science. They are considered one of the most important scientific awards in France. Xavier Blase’s distinction was one of two medals awarded in 2008 to researchers in the CNRS Department “Mathematics, Physics, Planets and the Universe”.

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At sufficiently low temperature, interacting electrons may crystallize and form a superstructure within their host atomic crystal. These ordering effects – of either charge or orbital type - consist of a long-wavelength modulation of the density and/or shape of the outermost occupied electronic shells. The complex interplay between various interactions gives rise to a great variety of different patterns such as checkerboards, ladders, or stripes. However, these are extremely difficult to observe experimentally because, typically, the ordering involves only one electron among hundreds. Nevertheless determining precisely which electronic orderings take place should help to describe the physics of an interacting many-electron system. The reward may be improved understanding of high-Tc superconductivity in cuprates or of colossal magneto-resistance in manganites, which are collective effects involving strongly interacting electrons and occur close to the onset of crystallizing phases.

The main experimental challenge is to overcome the low sensitivity of conventional X-ray or electron diffraction techniques. In fact, the standard crystallographic methods are hard-pressed to refine the positions of all the atoms involved in the electronic superstructure, and much less the orientations of their electronic orbitals. However a huge increase in sensitivity is achieved if X-rays of a special energy are used in diffraction experiments - a phenomenon known as “resonance”. In resonant diffraction, the energy of the incident photon is tuned to the energy of the photoelectric transition of one element, so that the photoelectron does not leave the crystal but visits (is promoted to) the valence orbitals. If the valence electron cloud has a different orientation from site to site, or a very small difference in density, one can observe a superstructure reflection, a so-called “orbital” or “charge order reflection”.

We performed resonant diffraction at the O K-edge of a manganite known to exhibit ordering of its 3d orbitals to see if the O 2p orbitals are involved in the 3d ordering. The O K-edge lies in the soft x-ray range (100-1000 eV) which requires a diffractometer in ultra high vacuum and a bright, energy-tunable X-ray beam. We used synchrotron radiation at the Swiss Light Source (Paul Scherrer Institut), and the soft X-ray scattering chamber built by the Institut Néel.

The diffracted intensity observed at the O K-edge provided evidence for ordering of orbitals on oxygen atoms doped with holes (Fig. 1). It allowed us to discuss recently proposed theoretical models, in particular those that assign an active role to the oxygen 2p orbitals in electronic and magnetic properties. Fig. 1 shows that there is ordering of O 2p orbitals hybridized with the Mn 3d orbitals but no ordering of the charge on the oxygen atoms at the wave vector of the Mn orbital ordering (which in turn was observed at the Mn L-edge).

The next step will be to compare O and Mn resonant scattering data to determine how many electrons or holes are shared, aiming to shed light on the magnetic exchange mechanism when electrons are hybridized between metal and ligand atoms. Further, we will then study how these properties evolve from the bulk of the material to its surface, and at the interface between systems with different order parameters.

The soft X-Ray diffractometer is open to external users, currently installed at the SIM beamline at the Swiss Light Source will be transferred to the Soleil synchrotron source, France, in 2009.

Further reading:

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NaI₃O₈, a Promising Material for Infrared Nonlinear Optics

The need for more efficient crystals in quadratic nonlinear optics has led us to explore the coordination chemistry of metallic iodates. During this study, we discovered a new NaI₃O₈ phase. This compound is among the rare materials having a very large range of optical transparency from the ultraviolet to the beginning of the far infrared (12.5 μm). It is thus very well adapted for applications in the windows of transparency of the atmosphere.

NaI₃O₈ crystallises in the acentric space group P₄. The crystal structure contains the novel oxo anion [I₃O₈]-, the first characterized polyiodate anion of pentavalent iodine (Fig. 1). This anion is formed by the condensation of three iodate anions in concentrated acidic solution. It contains three polarizable lone electron pairs, which favour high nonlinear optical susceptibilities.

We have grown single crystals of NaI₃O₈ with millimeter sizes (Fig. 2). This is a key progress for studies of the non-linear optical properties of crystals and for the development of device systems. Until now, among the metallic iodate compounds, only α-LiIO₃ has been available as the large single crystals required for full characterization of the non-linear properties.

Studies on powders have shown that NaI₃O₈ has good thermal stability (up to 350°C), high thresholds for optical damage (4.2 GW.cm⁻²), and high efficiency for Second Harmonic Generation qualitatively comparable to the efficiency of α-LiIO₃. The IR spectrum of NaI₃O₈ shows a wide window of transparency from 2.5 μm to 12.5 μm (Fig. 3). Contrary to α-LiIO₃ which has an absorption band at 6.5 μm and two other bands around 3 μm and 6 μm attributable to water, NaI₃O₈ is not hygroscopic and is as transparent in the two atmospheric transparency windows around 4 and 10 microns as all metallic iodates previously studied. This is a very important result since, at present, only two classes of non-linear optical materials - the chalcopyrites and the halides - present such good transparency. Since chalcopyrites are difficult to synthesize and halides are chemically unstable, we believe that the iodate family could be an alternative to these materials.

In summary, the new compound NaI₃O₈ is a promising material for infrared nonlinear optics, and moreover opens an interesting path to new chemistry.

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Further reading:
Electrochemical intercalation properties of nanocrystalline manganese dioxide

In nanometric materials, the surface can have a dominant role in determining the physical or chemical properties. This property is applied here to the domain of electrochemical intercalation, the basic mechanism for most rechargeable battery systems. The dramatic improvement in the electrochemical properties which has already been found for some negative electrode materials for lithium batteries (CoO etc.) is demonstrated in our work concerning proton intercalation in a simple material: tetragonal manganese dioxide or β-MnO₂.

The basic reaction here, similar to that used in most battery systems, is the reversible intercalation of an ion (H⁺) into the material, which is associated with oxido-reduction of the transition metal (Mn³⁺/Mn⁴⁺), thus: Mn⁴⁺O₂ + xH⁺ + xe⁻ ←→ HₓMₙ(4-x)+O₂.

A priori, β-Manganese dioxide is not a good intercalation material, because its tetragonal structure contains only narrow channels. So we have prepared this compound in nanometric form by two techniques, aerosol pyrolysis and extended milling. The first route of synthesis involves nebulising a manganese nitrate solution by ultra-sonic activation; the droplets formed are carried by a neutral gas flow to a furnace where they decompose into solid MnO₂. The grain size of the final product depends on the droplet size and on the gas flow. In the second technique, “standard” β-MnO₂ is ball-milled for various durations from 1 to 16 hours.

Transmission electron microscopy shows that “nano-MnO₂,” contains well-faceted grains with edges in the 20-50 nm range (Fig. 1). Analysis of X-ray peak widths gives clear evidence of a decrease in grain size (more exactly in the size of coherent diffraction domains) down to 20 nm for milling times ≥ 12 hours.

Controlled step-potential electrochemical studies in 1M KOH medium (Fig. 2) show a dramatic change in redox properties. On cell discharge (sweeping towards negative potentials with respect to a Hg-HgO reference electrode), macroscopic β-MnO₂ exhibits a unique reduction peak at -0.5 V, corresponding to the intercalation of 0.4 protons per MnO₂ formula unit (dashed line in Fig. 2a). The nanometric oxides, on the other hand, present a double reduction peak (Fig. 2b). The nanometric material is much superior to the macroscopic material in two important aspects. It has: (i) a higher reaction potential (main peak at -0.1 V) and (ii) a much higher electrochemical capacity (0.8 proton per formula unit). The variation in reaction potential is explained by invoking a surface energy term, which is related to the fact that surface manganese atoms have a lower coordination number and hence higher reactivity than bulk Mn atoms.

This work is performed in collaboration with several other labs, especially Etudes de Physico-Chimie et des Interfaces (LEPMI) of Enseeg-Inpg.

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