European Institute of Molecular Magnetism

THE YELLOW BOOK 2009

Services

- Advanced Instrumental Platforms
- Integrated Laboratories
- Consultancy

For further information info@eimm.org

Foreword

The **European Institute of Molecular Magnetism, EIMM** is a new organisation set up by the EU-funded Network of Excellence MAGMANet. It´s primary aim is to provide lasting integration of research and technological capabilities in the field of molecular magnetism and nanomagnets, crossing national and disciplinary boundaries. The institute integrates European research capacities into a powerful and durable framework acting as a reference point for Industry. The EIMM offers world class resources through a **Virtual Laboratory** of excellence and selected **Instrumentation Platforms.**

EIMM provides a unique consortium of European laboratories in the field of Molecular Magnetism and Nanomagnetism at the forefront of worldwide research in the area. It also provides a unique forum where industries can interact with scientists, stimulate research, access non-standard equipment and benefit from important technology transfer possibilities.

This booklet is the first edition of the guide to the EIMM services. Please note that it is available at the EIMM website http://www.eimm.org.

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ADVANCED INSTRUMENTATION PLATFORMS

ADVANPROCESS

ADVANCED PROCESSING TECHNOLOGIES FOR MICR- AND NANOSTRUCTURING MOLECULAR MAGNETS

ADVANPROCESS is a world class instrumentation platform, whose main objective is the development and application of innovative low cost processing technologies that are robust and easy to scale-up, for the preparation of molecular magnets with controlled micro- and nanostructure.

ADVANPROCESS endeavours to provide molecular magnets to different industrial sectors such as chemical, electronics, automotive, communications, pharmaceutical and medical sectors, bringing together expertise from molecular synthesis, material processing and nanostructuring, to molecular magnets physico-chemical characterization. ADVANPROCESS knowledge base consists of facilities as well as transferable expertise for the preparation of molecular materials with potential areas of application such as thin film sensors, electronics, data storage, nanomedicines, molecular light emitting diodes, spintronic devices, etc. This transferable expertise counts on experienced researchers with unique instrumentation and processing facilities for the preparation and characterization of molecular materials as films, micro- and nano-structured surfaces, micro- and nanoparticles.

This platform is cofinanced by *CSIC, UV, ITN* and *CIBER-BBN*, belonging to the *Instituto de Salud Carlos III*. *CIBER-BBN* is a Virtual Networking Biomedical Research Center in Bioengineering, Biomaterials and Nanomedicine, which brings together some of the leading Spanish research groups on the subject, including both universities and hospitals or

other technological centres. Its purpose is to conduct translational research and to transfer the results of the said research to industry. CSIC and CIBER-BBN (1-01-2008) have an agreement for the creation of an instrumental platform devoted to the processing and nanostructuration of molecular biomaterials.

For More Information:

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Instrument Layout

A) 50 and 300 mL lab-scale high pressure plant

Characterisitics

Lab-scale high pressure plants, based on a 50mL and 300mL stirred high pressure autoclaves equipped with pumps for the supply of compressed fluids and liquid solutions, respectively. Both plants could also optionally be equipped with several filters, manometers, thermocouples and back pressure regulators. The maximum operative pressure is 23MPa and the maximum operative temperature is 200ºC.

The 300mL plant is also equipped with a mass flow meter, and a data acquisition system.

Both plants have been designed for micro - and nanostructuring molecular and soft materials.

Instrument Layout

B) High pressure phase analyzer (CSICBarcelona)

Characteristics

This equipment allows the observation and measurement of phase equilibria in liquid and gas systems at high pressure.

Applications:

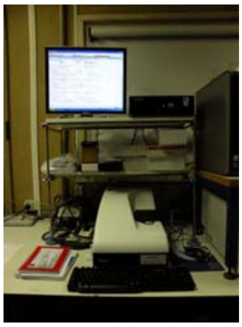
- Molecular materials solubility in compressed fluids.
- High pressure phase transformation analysis in dispersed systems (micelles, vesicles, suspensions, etc.)

This information is essential for the right development of compressed fluids based processes.
The instrument operates in either constant pressure and variable pressure mode with the following instrumental operational ranges:

Characteristics	Instrument Layout

C) Particle size measurement by light scattering (CSIC-Barcelona)

Measurement of the particle size distribution of solid or dispersed materials (suspensions, liposome, vesicles, emulsions), in the particle size range between 0.6nm and 6 microns, by dynamic light scattering.



Characteristics	Instrument Layout

D) Optical microscope equipped with a hot plate (CSIC-Barcelona)

Optical microscope for the observation of solid and liquid samples at a scale higher than 0,5 microns. This microscope is equipped with a hot plate, which enable optical visual inspection of material's transformations when heated (polymorph phase transformations, supramolecular rearrangements, etc..).

Characteristics	Instrument Layout

E) Microwaves (ITN-Portugal Node)

Performance of "cool reactions" where energy is applied directly to the reactants; the bulk heating is minimized by use of simultaneous cooling.

Applications:
• Synthetic procedures using reactants sensitive to termal degradation

Instrument Layout	Characterisitics

F) High vacuum thermal molecular evaporator (UV-Valencia)

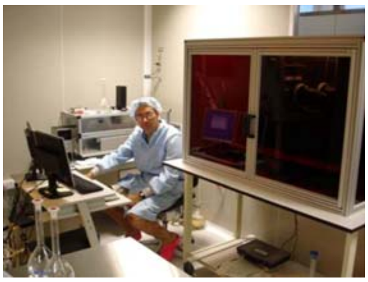
Molecular evaporator with two sources integrated in an inert atmosphere glovebox. Evaporated films, for this the molecules need to be thermally stable up to their sublimation temperature in low pressure (1.10-6 mbar).

Instrument Layout	Characterisitics

G) Spincoater inside a laminar flow Hood (UV-Valencia)

Spincoated films, this is a very flexible technique it basically only requires that the materials are soluble and do not crystallize rapidly.

Instrument Layout	Characterisitics



h) Langmuir Blodgett (LB) coater (UV-Valencia)

LB films, the material needs to form a molecular layer on water, usually requires molecules with a polar and an apolar part.

Characteristics

i) Photoresponse test equipment integrated in an inert glovebox (UV-Valencia)

Determination of the conductivity, charge carrier mobility, electro-emission and photoresponse

Instrument Layout

Platform Teams

CSIC-Barcelona Node (Spain)

Name	Surname	Phone	Email	Function
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Henk	Bolink	+34 96 3544415	henk.bolink@uv.es	Co-responsible.

ITN- Lisboa Node (Portugal)

Name	Surname	Phone	Email	Function
Manuel	Almeida	351 219946171	malmeida@itn.pt	Responsible .

Services

- Micro- and nanoparticulate pure molecular with homogeneoussupramolecular organizations (i.e. polymorphic phase, polymer foldings, etc..
- Particulate polymeric matrix loaded with molecular magnets
- Micellar and vesicular systems loaded with molecular magnets
- Porous materials, either crystalline or amorphous, with defined porosity and porous size.
- Nanostructured surfaces
- Amorphous mono- and multilayer films
- Self-assembled monolayers (SAMs)
- Optical observation of polymorphic phase transitions
- Particle size measurement
- Film characterization tools, ranging from morphological to detailed electronic properties, including a profilometer, AFM, STM,
- Film physical properties measurement system (PPMS).
- Opto-electronical thin film characterization measurement unit integrated in a inert glovebox : conductivity, charge carrier mobility, electroemission, photoresponse
-

Selected Examples

For selected examples please see experimental results published:

References
Micro- and nanostructuring with compressed fluids:

Articles

- N. Ventosa, S. Sala, J. Torres, J. Llibre, J. Veciana, "Depressurization of an Expanded Liquid Organic Solution (DELOS): A New Microparticle Production Technique" *Cryst. Growth Des*. 2001, *1*, 299-303

- M. Gimeno, N. Ventosa, J. Veciana, Y. Boumghar, J. Fourier, I. Boucher "Micronization of the Chitosan Derivatives D-Glucosamine Hydrochloride and D Glucosamine Sodium Sulphate Salts by Dense Gas Anti-solvent Precipitation Techniques", *J. Supercrit. Fluids* 2006, *38*, 94-102

- M. Gimeno, N. Ventosa, S. Sala, J. Veciana. "Use of 1,1,1,2-Tetrafluoroethane (R 134a) Expanded Liquids as Solvent Media for Ecoefficient Particle Design with DELOS Crystallization Process" *Cryst. Growth Des.* 2006, *6*, 23-25.

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- Cano-Sarabia M., Ventosa, N., Sala, S., Patiño C., Arranz R., Veciana, J "Preparation of Uniform Rich Cholesterol Unilamellar Nanovesicles Using CO2 Expanded Solvents" *Langmuir*, 2008, *24*, 2433

- Maria Muntó; Nora Ventosa; Jaume Veciana "Synergistic solubility behaviour of a polyoxyalkylene block co-polymer and its precipitation from liquid CO2-expanded ethanol as solid microparticles" *J. Supercrit. Fluids.* doi: 10.1016 J.SUPFLU.2008.07.019

Selected Examples Continued...

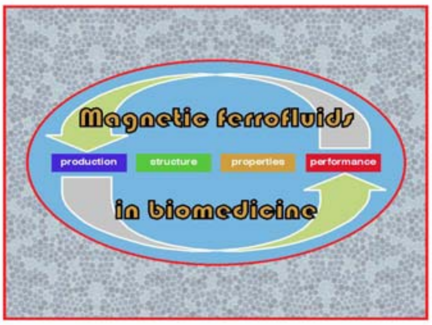
Patents

- Nora Ventosa Rull, Jaume Veciana Miró, Concepción Rovira Angulo, Santiago Sala Vergés. “Method for precipitating finely divided solid particles” Patent family numbers: ES2170008, EP 1314465, US7291295, CA 2426449, AU 8406501.
- Nora Ventosa, Jaime Veciana, Santiago Sala, Maria Cano. “Method for obtaining Micro- and Nano-disperse systems” Patent family numbers: ES2265262, WO2006079889, EP 1843836, US2007259971, CA2566960.

Nora Ventosa, Jaime Veciana, Maria Muntó, ”Obtaining micro-/nanoparticulated composite” Patent family numbers: ES2292300, WO2007009986

NAN04I+MT

Assessing Magnetic Nanoparticles For Magnetic Resonance Imaging and Magnetothemia



NANO4I+MT is a world class instrumentation platform comprising of unique instrumental portfolio to investigate the properties of magnetic nano-objects, either high spin molecules, clusters or particles and ferrofluids, to be used for Magnetic Resonance Imaging (MRI), NMR relaxometry and Magnetothermia applications.

For these studies, a NMR relaxometer and magnetothermal equipments are available and as the magnetic response of these materials takes place at excitations in the radiofrequency range, ac susceptometry is also included in the platform. These techniques are thought as important coming tools for diagnosis and therapy of different diseases in nanomedicine, particularly when the particles are vectorised and directed to target cells. In terms of collaboration, the Platform is opened to interested groups and industries requesting to use these equipments for specific experiments or to assess the interest of specific magnetic nano-objects. The instruments are located in three different laboratories, Zaragoza, Milano-Pavia and Florence, and experiments can be carried out either in individual instruments or in the whole instrumental manifold.

For More Information:

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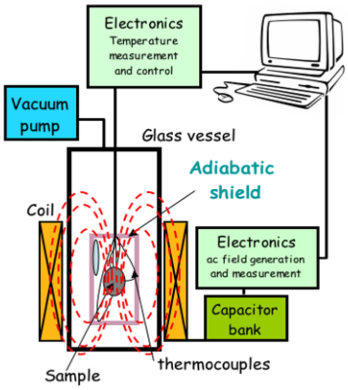
Instrument Layout

A) Magnetothermia



Characterisitcs

The specific absorption rate, SAR, is the standard parameter for estimating the heating efficiency. It can be measured with absolute precision thanks to a unique adiabatic magnetothermal setup. The enhancement of bioferrofluid performance in theranostics follow a fine understanding of its governing physical principles. They can be studied in NANO4I+MT with the same magnetic conditions used for clinical application.

The instrument operates in either adiabatic and non-adiabatic modes with the following instrumental operational ranges:

H = 0 – 5 kA/m
ν = 100 kHz
T = 300 K

Instrument Layout

b) Nuclear Magnetic Resonance (NMR) wide-band spectroscopy and relaxometry

Characteristics

The - NMR wide band and FFC (fast field cycling) equipments are devoted to different scientific issues, roughly grouped in 2.

The efficiency of novel MRI contrast agents can be established by measuring the standard parameters, i.e. the transverse r_2 and longitudinal r_1 relativities. With the current equipment these parameters can be measured in a wide range of frequencies (i.e. magnetic fields) on different nuclei, reproducing also the cases of clinical application.

All the solid state systems either in form of powders, solution or single crystals, can be studied as a function of frequency (magnetic field H) and temperature in wide ranges, useful also to connect classical to quantum world.

The instruments operate in the following ranges :
H = 0-9 Tesla
ν = 4 MHz – 380 MHz and 10 KHz-10 MHz (FFC instr.)

Characteristics

The efficiency of MRI contrast agents (CA) and the comparison among MR images with and without CA's, are studied through a low-field (0.2 Tesla, Esaote) imager. Here, the tests over in vitro model can be performed thus arriving to the final form of low-field investigation. Strict collaborations with a high-field imager (4.7 Tesla) research group of Milano and with several hospitals external to the Platform, will be used to assess the final results possibly in clinical and preclinical cases.

Instrument Layout

c) Magnetic Resonance Imaging (MRI)

Characteristics

As both the heat release and the contrast efficiencies of superparamagnetic based materials critically depend on the relaxation dynamics, the characterisation of the different parameters determining the reversal process is of crucial importance.

To this purpose a set-up to measure ac magnetic susceptibility in the frequency range of interest for clinical applications (50-500 kHz) has been developed.

The ac coils are inserted in an Oxford Instrument cryostat which allows temperature control in the 1.4-350 K range. The instrumentation integrates an already existing one operating in the lower frequency range (up to 25 kHz), thus offering an important tool for the complete characterisation of the reversal spin dynamics in single domain nanoparticles as well as in single molecule or single chain magnets.

The instrument operates in the following ranges:
Frequency: 50 - 500 kHz
Temperature: 1.4 → 350 K
Static field: 0 – 12 Tesla

Instrument Layout

d) High Frequency AC Susceptometer

Platform Team

Instrument Magnetothermia				
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INSTRUMENT: High Frequency AC Susceptometer				
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Applications

- Design of magnetic nanoparticles as MRI contrast agents
- Determination of the specific absorption rate (SAR) of magnetic nanoparticles
- Determination of nuclear relaxivities of paramagnetic and superparamagnetic contrast agents
- Determination of NMR spectra, transverse and longitudinal relaxation rates in solid state samples
- Characterization of the relaxation dynamics in a wide frequency range (from 0.1 Hz to 500 kHz)

Selected Examples

For selected examples please see the following experimental results published:

References

Accurate measurement of the specific absorption rate using a suitable adiabatic magnetothermal setup.
E. Natividad, M. Castro and A. Mediano
Appl. Phys. Lett., **92**, 093116 (2008)

Adiabatic versus non-adiabatic determination of specific absorption rate of ferrofluids.
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Magnetic Hyperthermia (general and applications)
Rudolf Hergt and Wilfried Andrä, *"Magnetic Hyperthermia and Thermoablation", in "Magnetism in Medicine: A Handbook",* Second Edition edited by Wilfried Andrä and Hanna Nowak, Wiley-VCH Verlag and Co., 2007, p. 550.

Andreas Jordan, Klaus Maier-Hauff, Peter Wust and Manfred Johannsen*, "Nanoparticles for Thermotherapy",* in Nanotechnologies for the life Science Vol 6: *"Nanomaterials for Cancer Therapy"* edited by Challa S.S.R. Kumar, Wiley-VCH Verlag GmbH and Co., 2006, p. 242.

Q.A. Pankhurst, J. Connolly, S.K. Jones and J. Dobson, J. Phys. D: Appl. Phys. 36 (2003) R167-R181.

Selected Examples Continued ...

Basic NMR and MRI

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- P.A.Rinck (ed.), "Magnetic Resonance in Medicine", 3rd edition, Blackwell (Oxford, 1993); C.Guy, D.Ffytche in "An introduction to the principles of medical imaging", Imperial College Press eds. (London, 2000)
- A. Lascialfari and M. Corti, in *NMR-MRI, ISR and Mossbauer Spectroscopies in MolecularMagnets*, ed. P. Carretta and A. Lascialfari, Springer-Verlag, Italy, 2007, p. 89.

Fast field cycling technique

- G. Ferrante and S. Sykora, Adv. Inorg. Chem., 2005, 57, 405

Contrast agents reviews

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- S. Aime, M. Botta, M. Fasano, S. Geninatti Crich and E. Terreno, Coord. Chem. Rev., 1999, 185–186, 321
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- S. Laurent, et al., in NMR-MRI, mSR and Mossbauer Spectroscopies in Molecular Magnets, ed. P. Carretta and A. Lascialfari, Springer-Verlag, Italy, 2007, p. 71
- Sophie Laurent, Delphine Forge, Marc Port, Alain Roch, Caroline Robic, Luce Vander Elst, and Robert N. Muller, Chem. Rev. 2008, 108, 2064–2110

NMR on molecular nanomagnets review

- F. Borsa, A. Lascialfari, Y. Furukawa, in: J. Dolinsek, M. Vilfan, S. Zumer (Eds.), Novel NMR and EPR Techniques, Springer, Berlin, Heidelberg, 2006. pp. 297–349
- F. Borsa, A. Lascialfari and Y. Furukawa, Inorganica Chimica Acta 361, 3777 (2008)

Applicative FFC (recent)

- Magnetic and relaxometric properties of Mn ferrites, A. Boni, M. Marinone, C. Innocenti, C. Sangregorio, M. Corti, A. Lascialfari, M. Mariani, F. Orsini, G. Poletti and M.F. Casula, J. Phys. D: Appl. Phys. 41, 134021 (2008)
- Cyano-bridged coordination polymer nanoparticles with high nuclear relaxivity: toward new contrast agents for MRI, Y. Guari, J. Larionova, M. Corti, A. Lascialfari, M. Marinone, G. Poletti, K. Molvinger and C. Guerin, Dalton Trans., 3658 (2008)

NANOMAGN

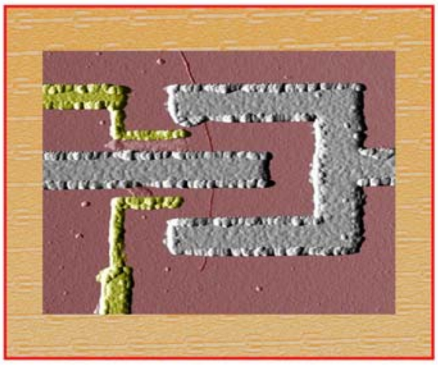
Magnetometry for single nanomagnets.

NanoMagn is a world class instrumentation platform developing small and highly sensitive magnetometers to detect extremely small magnetic flux.

Hall probes are based on semiconducting heterostructures (typically Al or In GaAs) of typical size of 10 to 1 mm. Using advanced lithography, probes with size down to 0.1 mm are also fabricated. Typical magnetic field sensitivity range between 10^{-6} to 10^{-8} T/√Hz below 100K. For probes with lateral size of 1mm, the magnetic flux sensitivity is typically $10^{-4}\Phi_0$.

SQUID made of 2 Josephson junctions shows a flux sensitivity of 10^{-5} F_0 when averaging I_{sw} during 1s at a rate of 10 kHz. This magnetometer allows to measure magnetic nano-crystals.

In terms of collaboration, the Platform is opened to interested groups and industries requesting to use these equipments for specific experiments or to assess the interest of specific magnetic nano-objects. The instruments are located in two different laboratories, Modena (I) and Grenoble (F), and experiments can be carried out either in individual instruments or in the whole instrumental manifold.



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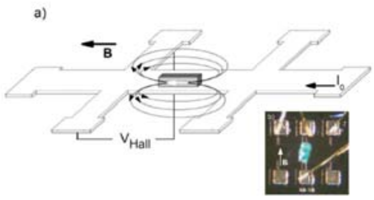
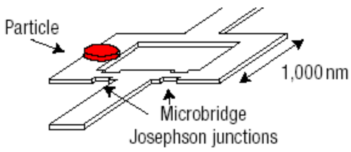
Instrument Layout

A) Hall nanoprobes



B) micro SQUID



Characterisitics

Flux magnetometry is used for advanced material characterization when very small crystals are available. It can be used as bio-sensor to detect systems (beads) with magnetic markers.

Hall probes are very flexible and can be used in different conditions: wide temperature (0.01 to 300K) and magnetic field (20T) range and in presence of e.m. radiation and light.

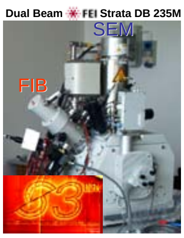
A worldwide unique equipment: the microSQUID magnetometer which is 10^{10} times more sensitive than a conventional SQUID.

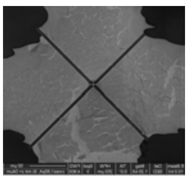
Instrument Layout

Characterisitics

Cryomagnetic system:
0.3 K$\rightarrow$ 400K
0 $\rightarrow$ 7 T
Rotator for
studying the
angular dependence

Instrument Layout





Characterisitics

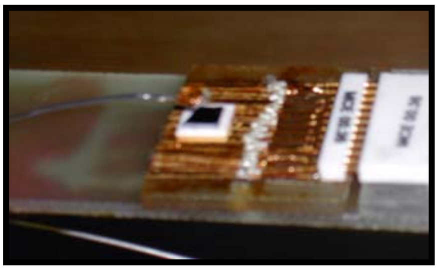
Facilities for nano-patterning
Electron beam lithography
Focused Ion beam
To fabricate Nanodevice

Characteristics

Fast Hall micro-probe.

For magnetic measurements under microwave radiation.

Instrument Layout

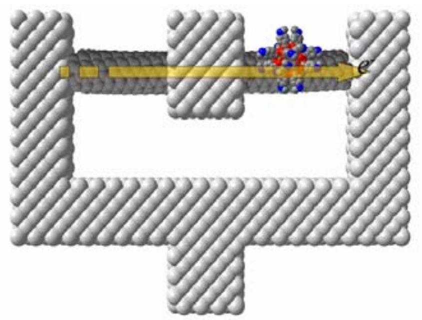


Characteristics

Superconducting Quantum Interferometer SQUID:

so sensitive to detection the magnetic moment of one single molecule (100 mB) .

Instrument Layout

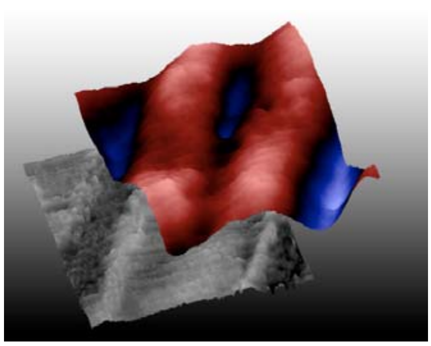


Characteristics

Scanning Hall probe Microscopy.

For imaging magnetic surfaces
2 K⟶ 300K
0 ⟶ 7 T

Instrument Layout



Platform Team

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Applications

- Magnetic characterization of micro- and nano-crystals.
- Determination of resonant microwave absorption by magnetic nanoparticles.
- Determination of magnetization dynamics in nanocrystals.
- Magnetic Imaging of thin films and surfaces.

Selected Examples

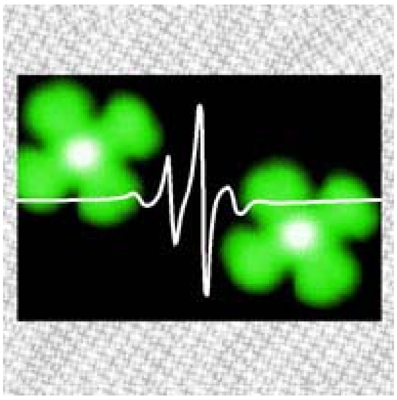
For selected examples please see experimental results published:

- Hall nano probes fabricated by Focused Ion Beam. A.Candini, M.Affronte, A. Di Bona, G.C.Gazzadi, D.Ercolani, G.Biasiol, L.Sorba Nanotechnology 17 (2006) 2105-2109
- Magnetic imaging of prussian blue nanoparticles grafted on FIB-patterned substrates. A. Ghirri, A. Candini, M. Evangelisti, G. C. Gazzadi, M. Affronte, F. Volatron, D. Brinzei, B. Fleury, L. Catala, C.David and T. Mallah, to appear in SMALL. DOI: 10.1002/smll.200800897
- Magnetization dynamics in the single-molecule magnet Fe8 under pulsed microwave irradiation, K. Petukhov, S. Bahr, W. Wernsdorfer, A.-L. Barra et V. Mosser Physical Review B 75, 064408 (2007)
- Carbon nanotube superconducting quantum interference device J.-P. Cleuziou, W. Wernsdorfer, V. Bouchiat, T. Ondarc¸ and M. Monthioux Nature Nanotechnology vol 1, p.54 october 2006

Singlemo

SINGLE MOLECULE LOCAL PROBE SPECTROSCOPIES

SINGLEMO is a world class instrumentation platform comprising unique STM instruments dedicated to the investigation of single molecules by local probe spectroscopies. The underlying technologies combine the unrivaled spatial resolution of STM with peculiar spectroscopic tools for atomic and molecular recognition based on the electric and magnetic properties of the investigated materials.



SINGLEMO joins together expertise in the use and development of high-tech instrumentation with the ability of preparing and characterizing single functionalized organic and inorganic magnetic molecules and molecular magnetic ultrathin films.

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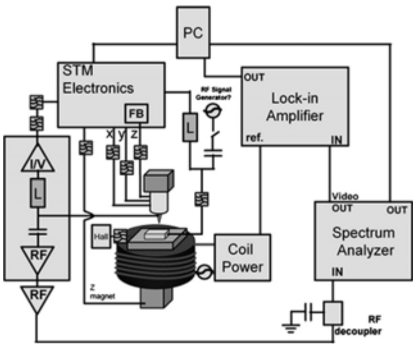
Instrument Layout

A) ESN (Electron Spin Noise) STM (Scanning Tunnelling Microscope)



Characterisitcs

Spectroscopies related to STM tunnelling effect offer incomparable insights on local properties of conductive surfaces, due to the without equal lateral resolution of STM.

The peculiar goal of this instrument is the possibility to detect a signal associated to the Larmor precession of a localized electron spin in an external magnetic filed. The electron spin resides within an isolated paramagnetic molecule adsorbed on the metallic surface. The signal is searched by analysing the *rf* spectrum of the tunnelling current, while the tip is tunnelling over the molecule: in fact, the current may show a modulation at the Larmor frequency.

The technique opens the way to fundamental studies related to the physics of single spin detection.
Experiments have been successfully performed on a set of different radicals (DPPH, BDPA, NitronylNitroxides) adsorbed in sub-monolayers quantity on Au(111) by means of wet chemistry and tuned functionalization of the molecules.
The instrument was born as a prototype to study the feasibility of this novel technique. It works in air; the magnetic field can be set up to 200 G (range of detectable frequency is 100-1000 MHz). means of wet chemistry and tuned functionalization of the molecules.

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Characteristics

The Solver P47-PRO SPM is a universal tool for the complex research of different objects in air, liquid and controlled gas environments with sample heating up to 130°C. It permits to operate either in Atomic Force Microscopy (AFM) or in Scanning Tunnelling Microscopy (STM). Scanning-by-sample scheme realized in the microscope provides high resolution easy to exchange the SPM mode. It is suited for single -molecule investigation as well as high resolution spatial characterization of molecular monolayers, deposited nanoparticles and patterned films.

Operation modes
Microscopies:
In air/controlled atmosphere:
STM and Low Current STM (down to 3pA)
AFM(contact+semicontact+ noncontact)
Lateral Force Microscopy (LFM)/
Phase Imaging mode
Force Modulation mode/Adhesion/Force Imaging
Magnetic Force Microscopy (MFM)
Electrostatic Force Microscopy (EFM)
Scanning Capacitance Microscopy (SCM) Kelvin Probe microscopi (KPM)
Spreading Resistance Imaging (SRI)
In liquid:
Atomic Force Microscopy (AFM) (contact + semicontact + non-contact)
Lateral Force Microscopy (LFM)
Phase Imaging mode
Force Modulation mode
Adhesion Force Imaging.
Spectroscopies:
AFM (force-volume imaging, amplitude-distance, Phase-distance curves)
STM (I(z), I(V), Local Barrier Height
(LBH), Local Density of States (LDOS).
Lithographies:
In air:
By AFM-Force (scratching + dynamic plowing) and AFM-Current (DC & AC)) and by STM *In liquid:*
AFM (scratching + dynamic plowing).
Nano-manipulations:
Contact Force

Instrument Layout

B) P47-pro SPM

Characteristics

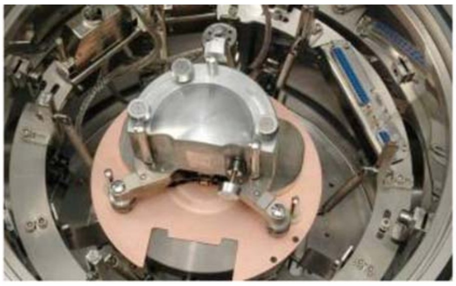
This partially home-made setup allows high-vacuum AFM and derived techniques such as MFM, EFM and different phase sensitive technique are available.

The open design setup allows further development of this apparatus. Owing to the high vacuum operation, it makes it possible to increase the cantilever sensitivity, thereby raising the accuracy of measurements of weak forces which is especially important on application of highly sensitive magnetic measurements, Kelvin probe microscopy and scanning capacitance microscopy.

Vibration-isolating system consists of a two-level passive vibration isolation.

Instrument Layout

B) P47-pro SPM



Characteristics

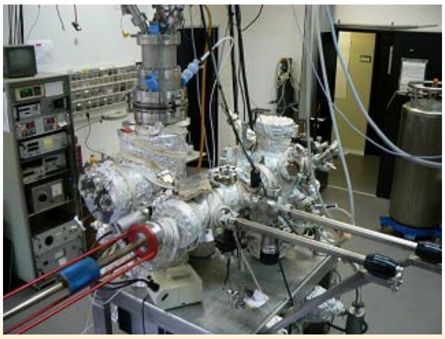
The LT-STM has been designed for the addressing of single atoms and molecular nano-objects adsorbed on conductive substrates.

The instrument can be used for measuring tunnelling current down to 2pA between a metallic tip and a functional molecule. The available temperature range is 2.8 K to 300 K. The apparatus allows to study in great detail the adsorption geometry of the molecules and some of their electronic and magnetic properties.

The LT-STM is coupled to a homebuilt UHV chamber that allows atoms and molecule deposition from newly developed evaporators onto *in*

Instrument Layout

C) LT-STM (Low Temperature Scanning Tunneling Microscope)



Characteristics

-*situ* prepared substrates. This chamber contains also specific setups for tip preparation.

The LT-STM instrument can also be used for spin polarized (SP) experiments. Within these SP-STM experiments the tunnelling current is measured using a magnetic tip and the spin signal is detected by recording the differential conductance as a function of sample voltage. This technique opens new opportunities for fundamental studies linked to the spin states of single molecules but also a way to explore the coupling of the molecular spin with magnetic substrates. The instrument has been already used for such measurements and has shows a high degree of stability.

The sample stage offers also the possibility of carrying out *in-situ* four probe resistance measurements.

Instrument Layout

The central part of the LT-STM

Characteristics

This special LT-STM (6K) is designed for performing field-dependent spin polarized spectroscopy on single atoms/molecules and nanostructures. In principle the instrument is able to conduct most of experiments listed above for the customized LT-STM. It is furthermore equipped with a vector superconducting-coil for magnetic fields in x- and z-direction (up to 2T) to tune magnetic states of the sample.

The microscope comprises a the LT-STM chamber under UHV which includes the coils, and an additional UHV chamber for sample and tip preparation.
The additional UHV chamber is equipped with atom and molecule evaporators as well as standard surface cleaning and analysis tools.

The LT-STM chamber and the sample stage are designed to allow optical access to the tip and surface but also for in-situ evaporation of atoms and molecules onto the sample when it is kept at cryogenic temperatures.

Instrument Layout

D) LT-STM with a Vector Magnetic Field (VMF)

- An overview of the LT-STM (Createc) with home built VMF coils

Characteristics

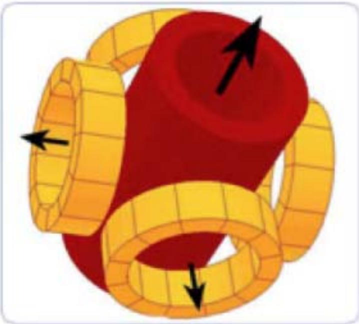
The scanning range of the microscope is 1 μm at 6 K with a low drift rate which does not exceed 0.2 nm per hour.

The LHe hold time is guaranteed for 48h without refilling the LHe cryostat.

The instrument was designed with a special sample stage placed in between the LN2 and the LHe radiation shield for the pre-cooling of the substrate and for molecules/atom deposition at low temperatures.

Instrument Layout

- the vector field coils configuration



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Applications

- Single spin detection as a tool of identification/chemical characterization of paramagnetic species on a conductive surface. (ESN-STM)
- Morphology characterization of conductive and non conductive surfaces.
- Detailed SPM characterization of organic and inorganic ultra-thin films
- Design and characterization of Self-Assembled monolayers at the molecular-resolution level.
- Characterization of Single Molecule Magnets monolayers and Sub-Monolayers
- STS on air preliminary investigations of molecular adsorbates.
- - Spin-polarized tunneling and transport through single magnetic objects: atoms, molecules and small nanostructures.
- - Identification of adsorption geometry, conformation and coupling of single magnetic objects at surfaces.
- - Magnetic field-dependent spectroscopy and manipulation of the spin state.
- - Study of conformation and dynamic of single molecules on surfaces.
- - Design of artificial nanostructures by molecule and atom manipulation.

Selected Examples

For selected examples please see experimental results published:

ESN-STM

- Electronic spin detection in molecules using scanning-tunneling-microscopy-assisted electron-spin resonance, C. Durkan and M. E. Welland, Appl. Phys Lett.. 80, 458 (2002)
- Spin noise fluctuations from paramagnetic molecular adsorbates on surfaces, P. Messina, M. Mannini, A. Caneschi, D. Gatteschi, L. Sorace, P. Sigalotti, C. Sandrin, S. Prato, P. Pittana, Y. Manassen, J. Appl. Phys. 101, 053916 (2007)

Selected Examples Continued ...

- Addressing individual paramagnetic molecules through ESN-STM, M. Mannini, P. Messina, L. Sorace, L. Gorini, M. Fabrizioli, A. Caneschi, Y. Manassen, P. Sigalotti, P. Pittana, D. Gatteschi, Inorg. Chim. Acta 360, 3837 (2007).

- Towards the Detection of Single Polychlorotriphenylmethyl Radical Derivatives by means of Electron Spin Noise STM V. Mugnaini, M. Fabrizioli, I. Ratera, M. Mannini, A. Caneschi, D. Gatteschi, Y. Manassen, J. Veciana Solid State Sci. (2007) In press

Single Molecule Magnets characterization:

- *Isolated and Addressable Single-Molecule Magnets on Native Gold* L. Zobbi, M. Mannini, M. Pacchioni, G. Chastanet, D. Bonacchi, C. Zanardi, R. Biagi, U. Del Pennino, D. Gatteschi, A. Cornia, R. Sessoli Chemical Communications 12, 1640 (2005).

- *Advances in single-molecule magnet surface patterning through microcontact printing* M. Mannini, D. Bonacchi, L. Zobbi , F. M. Piras, E. A. Speets, A. Caneschi, A. Cornia, A. Magnani, B. J. Ravoo, D. N. Reinhoudt, R. Sessoli, D. Gatteschi. Nano Letters 5, 1435 (2005).

- *Solvent Effects on the Adsorption and Self-Organization of Mn12 on Au(111)* F. Pineider, M. Mannini, R. Sessoli, A. Caneschi, D. Barreca, L. Armelao, A. Cornia, E. Tondello, D. Gatteschi. Langmuir 23 (2007) 11836

- *Insertion of a functionalised Single Molecule Magnet into preformed self-assembled* monolayers F. Pineider, M. Mannini, C. Sangregorio, L. Gorini, R. Sessoli. Inorg. Chim. Acta 361 (2008) 3944.

- *XAS and XMCD Investigation of Mn12 Monolayers on Gold* M. Mannini, Ph. Sainctavit, R. Sessoli, C. Cartier dit Moulin, F. Pineider, M.-A. Arrio, A. Cornia, D. Gatteschi. Chemistry A European Journal 14, 7530 (2008).

- A. Naitabdi, J.P. Bucher, Ph Gerbier, P. Rabu, M. Drillon
  Self-assembly and magnetism of Mn12 nanomagnets on native and functionalized gold surfaces
  Adv. Materials, 17, 1612 (2005).

- M. Koepf, J.A. Wytko, J.P. Bucher, J. Weiss
  Surface-tuned assembly of porphyrin coordination oligomers
  J. Am. Chem. Soc. 130, 9994 (2008).

Selected Examples Continued ...

- A. Nait Abdi, J.P. Bucher, Ph Gerbier, P. Rabu, O. Toulemonde, M. Drillon
  Magnetic properties of bulk Mn12 Piv16 single molecule magnets and their self-assembly on surfaces
  J. Appl. Phys. 95, 7345 (2004).

Organic Radicals Characterization

- *An integrated approach to the characterization of self-assembled organic radicals on Au(111) surface*
  M. Mannini, L. Sorace, L. Gorini, F. M. Piras, A. Caneschi, A. Magnani, S. Menichetti, D. Gatteschi Langmuir 23, 2389 (2007)

- *Patterned monolayers of Nitronyl Nitroxide radicals*
  M. Mannini, D. Rovai, L. Sorace, D. N. Reinhoudt, A. Perl, B. J. Ravoo, A. Caneschi Inorg. Chim. Acta 361, 3525 (2008).

Nanoparticles Characterization

- *A New Route to Fabricate Monolayers of Magnetite Nanoparticles on Silicon*C. Altavilla, E. Ciliberto, D. Gatteschi, C. Sangregorio. Adv. Mater 17, 1084 (2005).

Spin Polarized (SP) STM

- *Visualizing the Spin of Individual Cobalt-Phtalocyanine Molecules*
  C. Iacovita, M.V. Rastei, B. Heinrich, Th. Brumme, J. Kortus, L. Limot, J.P. Bucher
  Phys. Rev. Lett. 101, 116602 (2008).

- Spin polarized tunneling on nanometer Co clusters by means of a Ni bulk tip
  M. Rastei and J.P. Bucher
  J. Phys.: Condens. Matter 18, L619 (2006).

STS of atomic and molecular clusters and islands

- *Surface electronic sates in Co nanoclusters on Au(111): Scanning tunnelling spectroscopy measurements and ab initio calculations*
  M. Rastei, J.P. Bucher, P.V. Ignatiev, V. Stepaniuk, P. Bruno
  Phys. Rev. B 75, 045436 (2007).

Selected Examples Continued ...

- Size-dependent Surface States on Strained Cobalt Nanoislands on Cu(111)
  M.V. Rastei, B. Heinrich, L. Limot, P.A. Ignatiev, V.S. Stepanyuk, P. Bruno, J.P. Bucher
  Phys. Rev. Lett. 99, 246102 (2007).

- Solitonic mass transport on metal surfaces induced by adatom clusters
  H. Bulou and J.P. Bucher
  Phys. Rev. Lett. 96, 076102 (2006).

- Grafting and thermal stripping of organo-bimetallic clusters on gold surfaces: a way towards controlled Co/Ru aggregates
  A. Naitabdi, O. Toulemonde, J.P. Bucher, J. Rosé, P. Braunstein, M. Drillon
  Chem. Eur. J. 14, 2355 (2008).

Magnetic force microscopy

- Nanoscale hysteresis loop of individual Co dots by field-dependent magnetic force microscopy
  M.V. Rastei, R. Meckenstock, and J.P. Bucher
  Appl. Phys. Lett. 87, 222505 (2005).

Experiments Schedule

The instruments are available for well defined measurements that are carefully planed and discussed in collaboration with the two host teams during a first contact. Reliable results are generally obtained within a well defined time slot. For experiments to be performed in UHV environment -instrument C) and D)- it is asked that the molecular systems are analyzed first by other techniques for thermal stability, vapor pressure, sublimation temperature, etc... Therefore, thermogravimetry (TGA) and mass spectrometry data should be collected beforehand since they cannot be performed by the host institution.

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