DEIMOS

Nanomagnets device integration:

study of the magnetization at the surface

At the nanometer scale, properties of matter start to diverge from those of the bulk, and size dependent effects come into play. Magnetism at the nanoscale is a fast growing area that attracts intense activity in both fundamental and applied research. As the scaling down process continues to advance, particle characterization becomes significantly more challenging or inadequate. At the cutting-edge in this domain the DEIMOS beamline offers magnetic measurement techniques based on polarized x-rays absorption thus allowing such challenging studies to be performed.

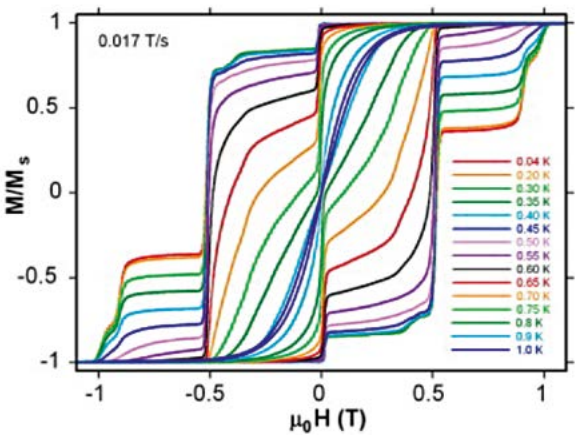


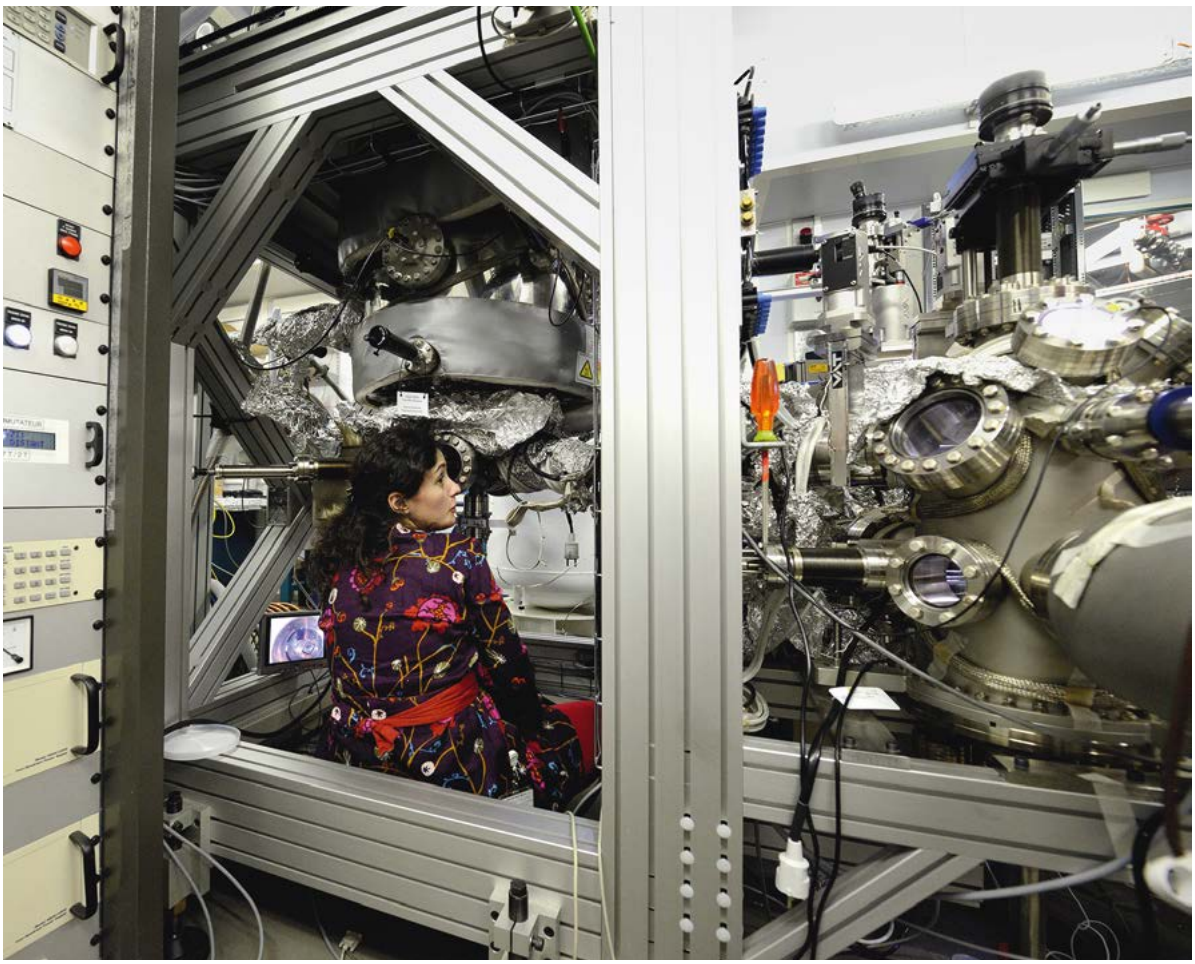
Figure 1. Magnetization curves (i.e. sample magnetization vs. applied magnetic field) of Fe_4 molecule magnet measured on single crystals by microSQUID magnetometry (with a magnetic field sweep rate of 0,017 Tesla/s and at temperatures ≤ 1 Kelvin). The presence of hysteresis curves demonstrates the magnetic bistability of Fe_4 at subKelvin temperatures; sharp steps in the hysteresis loops is a proof that the spin dynamic is dominated by quantum effects [ref.1]

As magnetic properties depend uniquely on both dimensionality and length scales, the exceptional magnetic properties of nanoparticles have put them at the forefront in the quest to develop the next generation of information storage technology, to improve cancer treatment and diagnosis protocols, as well as in environmental applications. However, standard magnetometric techniques only provide macroscopic information on the total magnetization of the objects measured. Moreover, they cannot discern between the contributions from the different elements present in alloys or multilayer systems. Also, the very small amount of materials present in such nano-structures requires a very sensitive measuring method.
Such measurements have become possible using the synchrotron based technique of x-ray absorption spectroscopy (XAS), in which the magnetic sensitivity is obtained by using circularly or linearly polarized x-rays (see insert).

Single Molecular Magnets

Single Molecular Magnets (SMMs) are the smallest existing nanomagnets. Made up of a small number of interacting spin centers (e.g. paramagnetic ions), this new class of fascinating magnetic material provides a unique opportunity to observe the coexistence of classical and quantum properties (see fig.1; ref.1). Indeed, while some possess magnetic ground states, they may also show quantum tunneling of the magnetization which could make them most promising candidates for nanoscale information technology based on the molecular spin state (ref.2). However, to achieve such technological innovation, and while these unprecedented quantum effects have been extensively investigated in bulk powders, they had first to be demonstrated by isolating them on a surface. The SMM community had to wait until 2009 for the first experimental evidence that SMMs isolated on a surface could exhibit so-called "memory effects" (ref.3). This collaborative work between the group of R. Sessoli (Department of Chemistry, University of Firenze, Italy) and Ph. Sainctavit (IMPMC-CNRS, Université Pierre et Marie Curie, France) demonstrated using XMCD (X-ray Magnetic Circular Dichroism, see insert) that a functional molecule (a tetrairon (III) clusters with a propeller-like structure, a.k.a. Fe_4) chemisorbed to form a single monolayer on a gold substrate, could show magnetic memory effects at the single-molecular scale, in addition to quantum effects bellow 1K.

This essential step towards the fabrication of molecular memory arrays was far from trivial and required the use of a linker (a carbon chain) to bind by chemical means the molecule to the gold surface, thus ensuring mono-



Edwige Otero, beamline scientist at DEIMOS, sitting underneath the "CroMag" setup.

layer coverage of the substrate. The challenge was then to measure such a minute amount of material at sub-Kelvin temperatures where quantum effects take place. For these measurements, the unique surface sensitivity of XMCD was pivotal.

In the continuation of this work, XNLD (X-ray Natural Linear Dichroism) was used to correlate the length of the linker with the structural ordering of the molecules chemisorbed on the gold surface. The researchers demonstrated the important discovery that short chains promote the growth of ordered films (ref.4). Also, as expected, the molecules with a higher structural order were also found to display higher magnetic ordering temperatures. This result paves the way towards SMM «device integration», but in this approach an important parameter to consider is the interaction that can arise between the molecule and the surface.

Towards quantum bits and molecular memristance

In order to accomplish this, the unique feature of the element selectivity of XMCD is used to explore simultaneously the magnetic properties and interactions of both the molecule and the substrate. In this continuous effort in engineering device suitable systems, functionalized $TbPc_2$ anchored to a silicon substrate (see fig. 2-a) was investigated at the DEIMOS beamline, and an unexpected enhancement of magnetic stability was observed (see fig. 2-b; ref.5). In these double decker lanthanide complexes (a class of SMM where one lanthanide atom is sandwiched between two phthalocyanine rings), such interplay between the molecule and substrate (gold, copper, nickel, silicon) has been used to tune the magnetic anisotropy.
It is hoped that such examples of fundamental approaches in research, used in order to understand the complex interplay between SMMs and materials (substrates), could ultimately succeed in the realization and fabrication of q-bits.

Another example of important work, with the ambition to realize a nanoscale molecular memory, is the first proto-

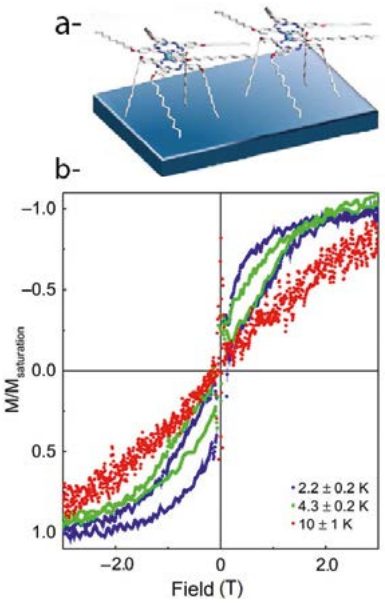


Figure 2.
a-Schematic representation of $TbPc_2(OC_{11}H_{21})_8$ molecules adsorbed on silicon by mean of 11 carbon atoms chains.
b-XMCD magnetization curves of a monolayer of $TbPc_2(OC_{11}H_{21})_8$ molecules assembled on silicon (recorded at M_5 edge and with a sweeping rate of 0,05Tesla/s) [ref.5].

type of memristance at the level of individual molecules demonstrated by Miyamachi and co-workers (ref .6). The authors were able to address individual molecules and to switch them between a combined high-spin/high-conduction state and a low-spin/low-conduction state. Adding such spin functionality to molecular switches is a key concept for realizing molecular spintronic devices.

→ **Contact:**
edwige.otero@synchrotron-soleil.fr

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X-ray magnetic circular dichroism (XMCD) was first observed in 1986 (one year after its theoretical prediction). It relies on the preferential absorption of left or right circular polarized x-rays by magnetic materials. Because XMCD is related to the spin state of the absorbing atoms, it thus probes the magnetic structure but also, as an energy dependent technique, the electronic configuration for each absorbing atoms present in the nanoparticle (i.e. it is an element selective technique). Moreover, in certain cases, XMCD can identify the different contributions to the magnetization, such as orbital and spin magnetic moments. Today, almost all synchrotron facilities around the world have dedicated beamlines for XMCD; at SOLEIL, the DEIMOS beamline has been optimized to perform XMCD in the soft energy x-ray range from (350eV to 2500eV). By probing only the first few nanometers of matter, soft x-ray XMCD has found its way into the community of magnetic nanomaterials, among them molecular magnets and organometallic complexes.

XMCD spectra are given by the difference between two x-ray absorption spectra (with the circular polarization vector orientated parallel or antiparallel to the external magnetic field). Thus, this technique is very sensitive to the x-ray beam stability (energy, flux and polarization) and reproducibility (the ability to repeat the same XMCD scan without altering the signal) is a key factor for a state-of-the-art XMCD beamline and which DEIMOS excels at. Moreover, at DEIMOS, the sample environment has been designed specifically for nanomagnetism case studies: it offers a magnetic field up to of 7 Tesla, a cryogenic sample stage (down to 1.5 K) and state-of-the-art sample preparation facilities including a glovebox, a MBE (molecular beam epitaxy) chamber and several in situ UHV characterization tools (such as variable temperature STM, a LEED (low energy electron diffraction) and an Auger spectrometer).