

♦ Effect of the Inorganic-Organic Interactions on the Outer-Layer Magnetic Structure in functionalized Magnetite-Based Nanoparticles

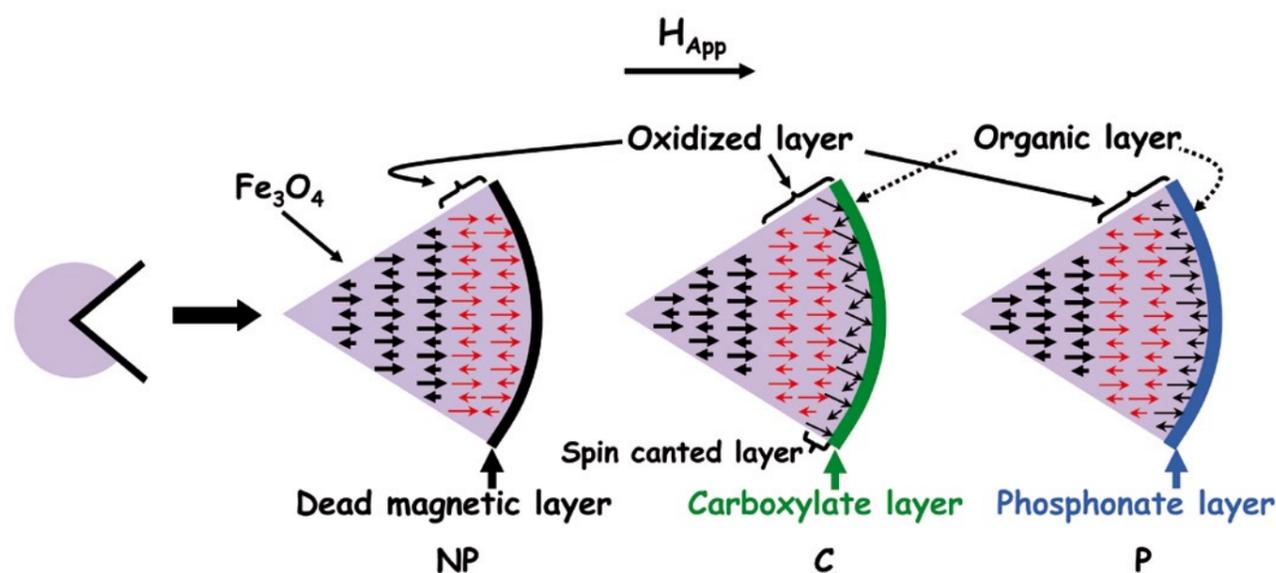
The control of the grafting of organic molecules on magnetic iron oxide is an important challenge for many applications in biomedicine or for bottom-up approach in devices elaboration. We investigated the grafting of lipophilic stilbene molecules through carboxylate or phosphonate entity on magnetite nanoparticles of 39 (± 5) nm in size. The starting magnetite based nanoparticles presents a mean composition, $Fe_{2.95}O_4$. Complementary in-field Mössbauer and SQUID measurements have demonstrated that the nanoparticles consist in a magnetite core surrounded by an oxidized layer. Phosphatation of magnetite with phosphoric acid was studied in a first step. It occurs rapidly by interaction with both positively charged groups and hydroxyl sites. Protonated binuclear species are identified as the main surface species; they are bound to the iron oxide

surface through Fe^{3+} in octahedral sites located in the most dense (111) plane. Then the grafting of stilbene molecules at the surface of iron oxide nanoparticles using either a carboxylate or a phosphonate group as coupling agent has been compared. Whereas phosphonate is covalently bound to the surface, carboxylate is linked through weaker interactions. Mössbauer spectra recorded at 300 and 77K suggest a global composition of $Fe_{2.82}O_4$ for the two types of functionalization. The oxidized shell exhibits a spin canting in the carboxylate case leading to a decrease of the net magnetization of the oxide nanoparticle. No canting occurs in the phosphonate case resulting in an increase of magnetization with respect to the bare nanoparticles. This is interpreted in terms of a higher magnetic surface order due to super-super exchange coupling between iron ions through the

phosphonate while carboxylate interactions limit the surface exchange bonds. This result is of primary importance to tune the magnetic properties of functionalized nanoparticles for biomedical and high density storage media applications. ■

Coupling Agent Effect on Magnetic Properties of Functionalized Magnetite-Based Nanoparticles T. J. Daou, J. M. Grenèche, G. Pourroy, S. Buathong, A. Derory, C. Ulhaq-Bouillet, B. Donnio, D. Guillon, and S. Begin-Colin, *Chemistry of Materials* **2008**, 20, 5869-5875.

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Schematic representation of the surface of as-prepared (NP), carboxylate (C) and phosphonate (P) coated nanoparticles in the presence of an applied magnetic field. Arrows depict the resultant ferrimagnetic moment.

IPCMS News

- **Publisher:** Marc Drillon - **Coordination:** Daniel Guillon
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Editorial

In this issue, the spotlight is directed towards some recent achievements of the IPCMS on magnetism and spin polarized transport properties of nanostructures. First, new perspectives in spintronics with the so-called «resistive switching effect» in specific Fe/Cr/MgO/Fe magnetic tunnel junctions are described. This switching effect can be combined with a TMR device to provide innovative systems with a four-level resistance device. Another highlight deals with the understanding of persistent currents in metal rings and cyclic molecules. This theoretical study represents the first justification of the Hückel's empirical law stating that cyclic molecules are aromatic when the total number of delocalized π electrons satisfies the relation $N=4n+2$ (with $n=0, 1, 2 \dots$).

One of the major challenges in molecular spintronics is the control of the spin-state of a single molecule. This is reported for the first time by an IPCMS team by using a low-temperature spin-polarized scanning tunnelling microscope (SP-STM), to measure the spin transport across cobalt phthalocyanine molecules adsorbed on cobalt nanoislands.

Finally, new hybrid materials based on magnetic iron oxide nanoparticles coated with lipophilic stilbene molecules are highlighted. It is demonstrated that phosphonate groups used as coupling agent between the oxide core and the organic shell have a major influence on the magnetic behaviour. Such a result is of primary importance to tune the magnetic properties of functionalized nanoparticles for biomedical applications, namely imaging and hyperthermia treatments.



Experimental setup for the fabrication of tunnel junction multilayers.

Marc Drillon
Director

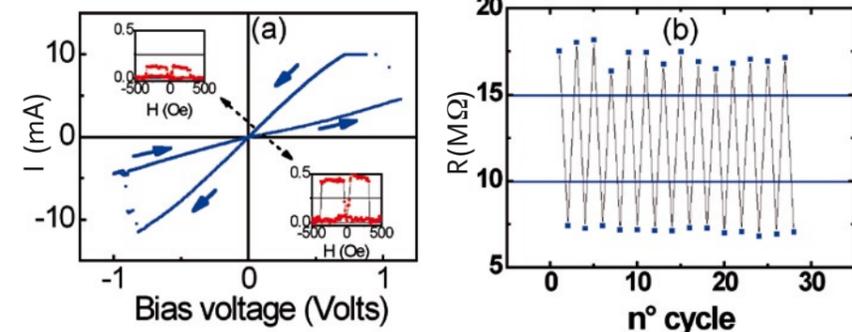
◆ Resistive “Switching” in epitaxial Fe/Cr/MgO/Fe magnetic tunnel junctions

We recently published in Applied Physics Letters results obtained on Fe/MgO/Fe junctions in which we inserted a few Cr atomic layers next to the MgO barrier. Chromium not only decreases the measured tunnel magnetoresistance (TMR) value but also leads to the so-called “resistive switching” effect. This effect has been studied for a few years especially in TiO₂ and in perovskites insulating films: the resistance switches from a high to a low value upon applying a stress voltage. The inverse effect is observed when changing the sign of the applied voltage. This makes “resistive switching” devices good candidates to elaborate a new type of memories. Nevertheless, the physical origin of this phenomenon remains unclear.

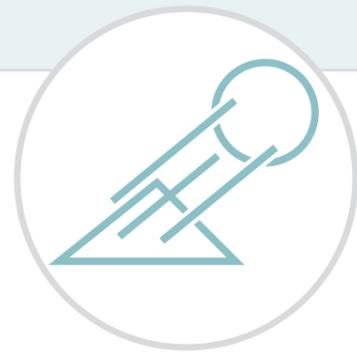
We observed at IPCMS that this switching effect could be combined with a TMR device, based on the well known epitaxial MgO barriers. Indeed, as shown on Fig. (a), the switching from a high to a low resistive state is correlated to a change of the TMR value which remains measurable in both states. Moreover, the switching effect appears as highly reproducible, as shown on Fig. (b) in which 30 cycles among 200 are presented.

We make the hypothesis that oxygen vacancies migrate in the MgO barrier, because

of the high electrical field across the barrier, leading to these switching effects. We suppose that oxygen vacancies are due to the partial oxidation of chromium at the interface with MgO. We moreover showed that the conductance is made through two different channels in parallel: on the one hand, the usual tunnel conductance through the MgO barrier leads to the TMR effect; on the other hand, the conductance across “hot spots” with oxygen vacancies leads to the resistive switching effect. This study could pave the way to the development of new systems with a four-level resistance device: two of them could be



(a) $I(V)$ curve measured on a Fe/Cr/MgO/Fe magnetic tunnel junction (lateral size: 10 μm) showing a resistive switching effect. Inset: evolution of the TMR in the high and low resistance states. (b) Resistive switching on a similar type of samples.



controlled by a magnetic field, and two of them by an electrical field. ■

D. Halley, H. Majjad, M. Bowen, N. Najjari, Y. Henry, C. Ulhaq-Bouillet, W. Weber, G. Bertoni, J. Verbeek, G. van Tendeloo Appl. Phys. Lett. **92**, 212115 (2008)

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◆ A new theorem for the sign of persistent currents in one-dimensional rings

Persistent currents flow in phase coherent rings that are threaded by a magnetic flux Φ . The magnetic field created by such a current is a paramagnetic or diamagnetic response to the external field, depending on the sign of the current. The understanding of the amplitudes and signs of persistent currents in metal rings and cyclic molecules remains however incomplete. A cornerstone in this domain is Leggett's theorem for N spinless fermions (fully polarized electrons) in one-dimensional rings with arbitrary potential landscape and electron-electron interactions. It states that the ground state energy $E(\Phi)$ assumes its maximum at zero flux (half a flux quantum $\Phi_0/2$) when N is even (odd). Since the persistent current can be expressed as

$I = -\partial F / \partial \Phi$ in terms of the free energy F , the maximum of $E(\Phi)$ at zero flux for even N implies a paramagnetic response of the zero-temperature persistent current. We have shown that the free energy $F(\Phi)$ assumes its minimum at $\Phi_0/2$ (zero flux) when N is even (odd). Those minima represent the counterparts of Leggett's maxima. Moreover, the new minima hold at finite temperature and for unpolarized electrons, when the numbers of electrons with spin up N_\uparrow and down N_\downarrow are both even or odd. They establish rigorously that the response of one-dimensional rings with odd N_\uparrow and N_\downarrow is diamagnetic. This justifies Hückel's empirical rule which postulates that cyclic molecules are aromatic when the total number of delocalized π electrons satisfies

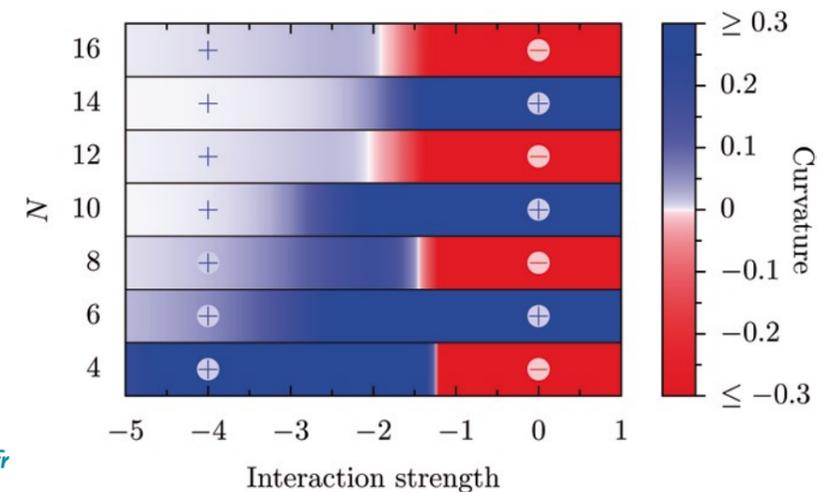
$N = N_\uparrow + N_\downarrow = 4n + 2$ with $(n = 0, 1, 2, \dots)$. For even N_\uparrow and N_\downarrow , the low flux response is not determined by the theorems. Only in the absence of interactions Leggett's maxima for the independent spinsystems imply a paramagnetic zero-temperature response. To illustrate the possible behaviour of the magnetic response, in the figure we show numerically obtained curvatures of $E(\Phi)$ at zero flux as a function of the interaction strength, for disordered Hubbard rings with unpolarized electrons. As dictated by our theorem, rings with $N = 4n + 2$ are always diamagnetic (positive curvature, blue). For $N = 4n$ the response is paramagnetic (negative curvature, red). Strong enough attractive interactions

make the system diamagnetic and lead to a $\Phi_0/2$ -periodic current that is characteristic of superconducting rings. ■

This work has been performed in collaboration with physicists from Saclay, Grenoble and Karlsruhe.

X. Waintal, G. Fleury, K. Kazymyrenko, M. Houzet, P. Schmitteckert, D. Weinmann, Persistent Currents in One Dimension: The Counterpart of Leggett's Theorem Phys. Rev. Lett. **101**, 106804 (2008)

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◆ Visualizing the Spin of Individual Cobalt-Phthalocyanine Molecules

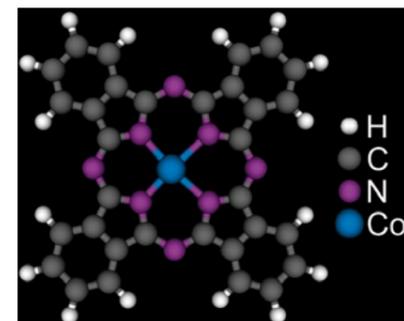
A team of the IPCMS, in close collaboration with theorists from the TU Freiberg, has visualized for the first time the spin of single molecules by exploiting an engineered nanoscale magnetic tunnel junction.

Molecular spintronics uses ferromagnetic electrodes to inject a spin-polarized current across molecules. Despite there is evidence that the molecule-electrode interface has a decisive impact on spin transport, little is known about the chemical and magnetic coupling between a molecule and a ferromagnet. A low-temperature spin-polarized (SP) scanning tunneling microscope (STM) has been employed in this regard to study for the first time the spin transport across single cobalt-phthalocyanine molecules adsorbed on well characterized cobalt nanoislands with perpendicular magnetization. Compared to other techniques, the location and number of adsorbates on the

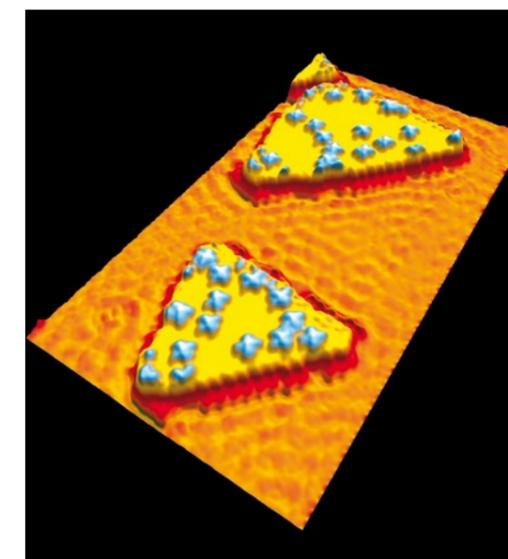
electrodes is perfectly known with STM. Furthermore, the SP electron tunneling can be characterized above an adsorbate, or over other locations of the surface, with atomic resolution. For cobalt-phthalocyanine in particular, a specific feature in the conductance spectrum taken above the cobalt atom of the molecule is exploited

to spatially resolve two stationary spin states. Such states correspond to the two possible “up” and “down” orientations of the molecular magnetization on the cobalt islands.

In the lowest energy configuration, the Co atom is found to adopt a bridge position with respect to substrate atoms, while the N atoms are responsible for the chemical bond with the surface. Calculation also shows that the states involved in the magneto-transport arise from the d_{z^2} , d_{xz} and d_{yz} orbitals of the molecule. The magnetization density reveals that the coupling between the molecule and the electrode is ferromagnetic with a direct contribution as well as an indirect superexchange contribution due to the particular configuration of the N atoms mediating the coupling with the surface. It is anticipated that control over the adsorption geometry, and ultimately over the spin conductance, can potentially be achieved by a careful choice of the ligands that bind the molecule to the surface. ■



Cobalt-phthalocyanine molecule.



CoPc molecules adsorbed on cobalt nanoislands grown on Cu(111). (a) Structure model for CoPc. (b) Three-dimensional STM image (40 x 20 nm, 0.1 V, 0.5 nA). The spatial oscillations on the Cu(111) surface are due to the scattering of the Shockley surface-state electrons.

C. Iacovita, M.V. Rastei, B. Heinrich, Th. Brumme, J. Kortus, L. Limot, J.P. Bucher, Phys. Rev. Lett. **101**, 116602 (2008).

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