Further measurements of the frequency dependent AC susceptibility showed that susceptibility exhibits well-defined maxima. For all samples, the maximum relative shift per decade of frequency is significantly larger than expected for a freezing, spin glass like mechanism, indicative of a relaxation mechanism dominated by single particle magnetic anisotropy rather than interaction between particles.

Moreover the relaxation time obeys the Néel-Brown model used for non-interacting NPs. Therefore, it can be definitely concluded that the blocking of the particle moments is mostly due to the particle magnetic anisotropy. The magneto-crystalline anisotropy constants, calculated in the three samples are larger than the anisotropy constant of bulk magnetite, evidencing a large influence of the surface on the magnetic properties (and on the nature of the grafting function). An important modification of the anisotropy constant is observed between NPs hybridized by carboxylateand phosphonate-based ligands and is explained by the difference of grafting functions. All these results stress the fact that the modifications of the magnetic proper-

(a)

(a)

ties of very small particles cannot be only related to dipolar interactions but also on the surface state and surface magneto-crystalline anisotropy of magnetic NPs too.

A. Demortière, S. Buathong, B. P. Pichon, P. Panissod, D. Guillon, S. Bégin-Colin*, B. Donnio*, Small 2010 6 1341-1346.

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• 3D self-connected microwire

Nematic liquid crystals are anisotropic liquids. Though they flow as ordinary liquids, they exhibit local order in the sense that their molecules are locally oriented along the same direction except for thermodynamic fluctuations. This structure is at the origin of interesting properties. We show here that, based on two of these particular properties, self-assembling of microwires directly connected to pre-designated electrodes can be performed. The process takes place in three dimensions and has no rival today.

First, the space between the substrates bearing two electrodes (P and Q) to be connected is filled with a nematic liquid crystal. The surfaces of the substrate being treated in order to force a conflicting orientation of the nematic in P and Q. In this manner, a disclination (i.e. a defect line or a topological singularity) takes place along a line that joins P to O. This first process defines the exact path where the microwire will be produced.

Then, another property of nematic liquid crystals is put to action, namely that colloidal particles immersed into a liquid crystal are dragged by a picoNewton force that arises from the elastic distortions they produce in their surroundings. So, polymer conductive colloids initially uniformly dispersed into the nematic liquid crystal

slowly move toward the disclination lines and are eventually trapped onto them. In this manner, a micronecklace is found in the place of the disclination line (Fig.1).

Finally, in a third step, a small quantity of pyrrole solved into the liauid crystal is electropolymerized on applying a voltage between P and Q. Neighbouring particles working as microelectrodes, polymerization takes place between them and after a few hours, they definitely stick together. The

necklace of particles turns into a cohesive microwire (Fig.2). Clearly, the wire's quality is not satisfactory yet, but this can be improved. In particular, the wire thickness may be reduced, for example, by decreasing the particles' size and concentration.

The process can be extended to produce a large number of microwires between substrates simultaneously, provided that they are not too close to one another. This could lead to the development of large-scale three-dimensional integrated circuits,



Fig.1: Self-assembled micronecklace. The bar on (b) is $30 \,\mu m$ long.



Fig.2: A microwire is finally produced by means of electropolymerization. A flow of the liquid crystal in the isotropic phase in the vicinity of the microwire proves its real materialization. The bar on (b) is $30 \,\mu m$ long.

giving the opportunity to Moore's law to escape in the third dimension.

J.-B. Fleury, D. Pires, Y. Galerne ; Phys. Rev. Lett. 103, 267801 (2009).

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Editoria

This workshop aimed at promoting partnerships between the three countries on nanostructured magnetic materials and advanced polymers. The presentations focused on the latest advances in the field of magnetic nanostructures, magneto-optical materials and spintronics materials, including hybrid multilayers and supramolecular architectures. The invited lectures have been delivered by a balanced number of scientists coming from USA, South Korea and France. They gave rise to fruitful discussions and to the establishment of several collaborative projects between the three countries. This workshop was made possible thanks to the Air Force Office of Scientific Research which initiated and supported this event.

4



No. 11



Left to right: Marc Drillon director IPCMS, Bertrand Girard director of Institut of Physics at CNRS, Mme Minh-Hà Pham-Delègue director of international affairs at CNRS and Jeong Weon Wu project coordinator at Ewha University.

Developing and strengthening international scientific cooperation with Asia is a major objective of the Institute. In the last few years, we have launched close partnerships with Ewha Womans University including common research, short and long term visits of PhDs and researchers and a regular Winter School on Nanosciences for PhD and master students. We have further been involved in a networking program with several universities in South Korea supported by CNRS that is about to start.

Last July, a collaboration project between IPCMS and the Physics Department of EWHA Womans University in Seoul has been selected by the National Research Foundation of Korea in a high level international competition to be funded in the next 6 years. The common project on quantum dynamics imaging of functional materials based on nanostructures aims at the understanding of topical issues in nanosciences, specifically in spintronics, spin-photonics, and quantum imaging applications, and at contributing to new advances in nanotechnologies.

A "Quantum Dynamic Imaging Research Centre" involving several teams of IPCMS and supported by the National Research Foundation of Korea and the Gyeonggi province will be created at Ewha University to strengthen collaborations and take advantage of complementary skills.

The first Asia-Europe summit for physics held in Tsukuba last April has recognized the importance of such relationships between our countries.

Marc Drillon, Director

UNIVERSITÉ DE STRASBOURO

on Nanostructured Magnetic Materials & Advanced Polymers Sponsored by AFOSR/EORD, July 19-22, 2010, Strasbourg, France





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• Ultrafast transfer of angular momentum in magnetic materials

How fast does it take to couple the orbital angular moments of the electrons to their spin moments in magnetic materials ? Recently, we have given an answer to this long waited question. From a fundamental point of view, it is known that the spinorbit coupling (SOC) plays a major role in the moment transfer. The SOC is a guantum interaction which is very important for practical applications like for example in the development of high density recording media. Indeed, a perpendicular magnetization can be induced in thin ferromagnetic films by controlling of the magneto-crystalline anisotropy which involves the SOC. It is therefore important to properly understand this interaction and in particular to know its dynamical behavior.

We have been able to measure the transfer of momentum by performing time resolved X-rays Magnetic Circular Dichroism (XMCD) experiments using the « femtosclicing beam line » at the BESSY synchrotron facility. We have shown that



Fig.1: Sketch of the time resolved XMCD experiment.

the change of the spin moment S_7 in ferromagnetic films is delayed by 60 fs with respect to a sudden change of the angular orbital moment Lz, using an ultrashort laser pulse. The experiment has been carried out in CoPd ferromagnetic films which have a perpendicular anisotropy. In addition, we could show that the relative decrease of the spin moment is larger than the orbital one. These results show that in « Femtomagnetism » experiments, where the change of the magnetization is induced by ultrashort laser pulses, it is the elevation of the electronic temperature associated to the SOC which is responsible for the ultrafast demagnetization.

Figure 1 shows a sketch of the time resolved XMCD experiment. The anisotropic distribution of magnetic moments, perpendicular to the film in the direction z, is represented by the ellipsoid. Two pulses are used to measure the dynamics of both projections L_z and S_z of the orbital and magnetic angular moments. The first one (the pump) is a near infrared laser pulse at 790 nm with a duration of τ_{Pump} of 60 fs. which is used to modify the electronic distribution by interband and intraband absorption optical processes. The second one is a femtosecond X-ray pulse, with duration $\tau_{Probe} \sim 100$ fs, which is used to probe the CoL_2 and CoL_3 edges of the 50 nm thick CoPd free standing film on a Si_3N_4 membrane. A variable time delay between the two pulses allows obtaining the dynamics of the projections $L_z(t)$ and $S_z(t)$ using the well known sum-rules used in static XMCD.

Figure 2 displays the main results of the experiment. The dynamics of $L_z(t)$ and $S_z(t)$ are represented in Fig. 2a) as well as the corresponding fits obtained with causal functions modeling the thermalization dynamics of the spins and charges and their relaxation to the lattice. The decrease

of orbital angular moment occurs in 220 ± 20 fs while the spin moment decreases within 280 ± 20 fs. The time dependent ratio of the two quantities is shown in Fig. 2b), indicating a larger decrease of the S_z component. We attribute it to an ultrafast change of the magneto-crystalline anisotropy energy $E_{PMA}\approx -\xi$ L·S, where ξ is the spin-orbit coupling parameter, due to the rapid heating of the electrons and mediated by the spin orbit interaction.



Figure 2 : Dynamics of the orbital L_z and spin S_z angular momenta.

(a): spin and orbital moments and corresponding fit with causal functions.(b): absolute ratio of the two momenta.

C. Boeglin, E. Beaurepaire, V. Halté, V. Lopez-Flores, C. Stamm, N. Pontius, H. A. Dürr, J.-Y. Bigot, Nature, **465**, 458-461 (2010).

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• In-situ observation of carbon nanotubes growth in an electron microscope

The conditions for the controlled growth of carbon nanotubes are still not known in sufficient detail to design facilities for the production of tubes with a pre-defined structure. Now, an *in-situ* electron microscopy study at the IPCMS has given insight into the growth mechanism of single-wall nanotubes. A composite of catalytically active transition metal nanocrystals and graphitic carbon has been subjected to intense electron irradiation in the heating stage of a transmission electron microscope. An intermixing of metal and carbon occurred to a certain degree by the sputtering of carbon atoms into the metal. Given the low solubility of carbon in the respective metal, the metal crystals were rapidly saturated with carbon. A focused electron beam was then applied to shape the metal crystal so as to form sharp tips. Once the tips had a radius of curvature below approximately 2 nm, the spontaneous nucleation and growth of single-wall



carbon nanotubes was seen to occur on these tips. The growth was accessible to real-time observation and was studied as a function of temperature. The illustration below shows an example where a carbonsaturated cobalt nanowire was thinned by electron irradiation until the double-cone metal broke at the bottleneck, leaving a growing carbon nanotube between the two metal tips.

Accompanying studies by atomistic computer simulations showed that the solubility of carbon in nanometer-sized metal particles depends on the size of the particles and decreases drastically if the diameter of the particle falls below 1-2 nm. Hence, carbon segregates on the sharp tips and crystallizes in the shape of nanotubes. These observations show that metal surfaces with high curvature are a necessary condition for the nucleation and growth of carbon nanotubes from metals. By structuring a metal surface so as to obtain arrays of hillocks with nanometer size, the goal of growing carbon nanotubes with a uniform structure could be achieved. The work

• Liquid Crystalline Ferrites

Ordered assemblies of monodisperse nanoparticles (NPs) that provide 2D or 3D superlattices constitute an attractive class of nanostructured functional materials for a wide range of potential applications. Various strategies have been used to elaborate periodic arrangements on micrometers scale of passivated NPs. Recently, an alternative strategy has been developed using mobile liquid crystalline (LC) phases by self-assembling quasi-spherical NPs capped with LC-forming agents. In contrast to other self-assembling methods limited to arrays of spheres, a higher modularity in the organization of covalent **LC-NP** hybrids is mandated by the self-healing ability and fluidity of the low-dimensional LC mesophases.

We have reported on the induction of a room temperature nematic phase for some mesogen-hybridized iron oxide NPs and on the modification of the surface magnetic anisotropy of NPs after surface derivatization.

The hybrids consisted of a magnetic iron oxide NP (\emptyset =3.3±0.7 nm) derivatized by proto-dendritic cyanobiphenyl-based ligands (LCi). Iron oxide NPs coated with oleate chains (NP@OA) were synthesized first. The partial substitution of the OA surfactants by LC1 and LC2 was then carried out by solvent-mediated exchange reaction. Both NP@LC1 and NP@LC2 hybrids Fig. 1: Schematic representation of the solvent-mediated ligand exchange reaction and chemical structures (LC1 and LC2).

develop birefringent and fluid textures reminiscent to that of a nematic phase, later confirmed by small-angle X-ray diffraction. The nematic-like phase may be pictured as a quasi-regular isotropic distribution of oxide nuclei within the organic matrix characterized by a local nematic order.

The temperatures below which the magnetic moments of the hybrids are blocked, NP@LC1 $(T_M~15K)$ and NP@LC2 $(T_M~12K)$, are unexpectedly lower than that of NP@OA $(T_M~18K)$, provisionally attributed to the decrease of the magnetic dipolar interactions. A more thorough analysis shows that the strength of the dipolar interaction, estimated as 3.3K, 1.7K and 2.2K for NP@OA, NP@ LC1, and NP@LC2 respectively, were too low to explain freezing temperatures above 10K.

Fig 2 : ZFC/FC curves (75 G) ► and hysteresis loops at 5 K (inset) of NP@OA, NP@LC1, and NP@LC2.



 Growth of a single-wall carbon nanotube at the breaking bottleneck between two cobalt crystals. Successive thinning of the wire is shown from the left to the right figure. The experiment was carried-out in-situ at 600°C in a transmission electron microscope.

has been carried out in collaboration with the catalysis group at the ECPM in Strasbourg who made the precursor materials and a theory group at the University of Helsinki.

J. A. Rodríguez-Manzo, I. Janowska, C. Pham-Huu, A. Tolvanen, A. V. Krasheninnikov, K. Nordlund and F. Banhart, Small **5**, 2710 (2009)

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