The endohedral metallofullerenes M@C_{60} are unique materials in which a positively charged core metal is offset-in a negatively charged strong carbon cage (Fig.1), with promising applications such as superconductors, organic ferromagnets and laser media.[1] A strong metal—cage interaction and intramolecular charge transfer from the metal atom to the carbon cage seems to be at the origin of unusual electronic and magnetic properties.

An interesting evolution of the magnetic moment has been reported using SQUID measurements: whereas in La@C_{60} the effective magnetic moment (µ_eff) of M^{3+} ion has been found larger than the theoretical one,[2] it appears dramatically smaller in heavy RE metallofullerenes M@C_{60} (e.g. Ho@C_{60}: 10.6 μB, theoretical Ho^{3+}: 9.5 μB). The general trend of the µ_eff decrease is that the higher the RE orbital moment (L), the larger the magnitude of the reduction. Indeed the carbon cage crystal field and orbital hybridisation may partially quench the RE orbital moment due to the very low symmetry.

Moreover in the endohedral metallofullerenes, the magnetic ordering could arise from metal-cage interactions and/or interfullerene metal-metal interactions through superexchange via the carbon cage.

A good way to understand the unusual behaviour of this new class of materials is to observe selectively the local electronic and magnetic structures of the encapsulated metal.

In this work, we concentrated first on the orbital contribution of the encaged-metal magnetic moment and on the magnetic ordering at low temperature between the metal centers by using X-ray magnetic circular dichroism (XMCD) in x-ray absorption (XAS) and on the endohedral metallofullerenes (M@C_{60}). We used the superconducting magnet on ID8 beamline at the European Synchrotron Radiation Facility (ESRF) as high field (up to 7T) and low temperatures (10K) were necessary. XMCD is routinely used to directly probe the ground state and spin (S) magnetic moments through sum rules,[4] and to determine the element selective magnetic ordering in a composite system.

XMCD has been performed at the RE M_{4,5} edges (3d→4f) on several M@C_{60} (M= Dy, Er, Ho) thin films deposited on Cu(111) substrate with various coverages (from <1 monolayer to multilayers). The 4f L moment has been investigated in order to study the influence of the carbon cage on the RE orbital moment and therefore the massive reduction of the total magnetic moment observed on the heavy RE-encapsulated. Gd@C_{60} has been used as a reference, as its electronic structure is well-determined and no effect from L will occur. The results will also be compared with atomic multiplet calculations.[5]

In parallel, temperature-dependent XMCD measurements and low-temperature hysteresis loops have established a paramagnetic coupling between the metal centers from 6K to 300K for all samples.

In addition, angle-dependent XMCD measurements have been performed at the M_{4,5} edges on M@C_{60} wedged films -starting from low coverages to bulk films- in order to investigate the magnetic anisotropy of M@C_{60} thin films. Indeed XRD and STM studies have revealed a molecular arrangement in a “head-to-tail” manner in crystals and on metal surfaces, which results from the permanent electric dipole moment along the symmetry axis of the M@C_{60} molecules.[6,7] We have tried to determine the direction of the easy-axis of magnetisation as a function of coverage and molecular arrangement, and to probe the anisotropy of the RE electronic states giving rise to the magnetic anisotropy.

Finally this study has been extended to higher coordinated metals inside the fullerene cage, presenting another molecular symmetry, such as M_{2}@C_{60}, (M= Dy, Er) and Ho_{2}N@C_{62} systems.[8] The first results will show if this different coordination of the RE ions inside the cage change the hybridisation between the cage and the metal, and provide different magnetic ordering and anisotropy. The comparison between M@C_{60} and M_{2}@C_{60} systems shed light on the competitive metal/metal-cage interactions.

This is the first XMCD study of these novel materials. The direct measurement of the encaged RE orbital moment and the isolation of the magnetic ordering of the ion inside the cage provide new information into the influence of the fullerene cage on the encapsulated metal and on the magnetic properties of these exotic systems.

References

Acknowledgements
C. De Nadai gratefully acknowledges Dr N. Tagmatarchis, Dr J. Dennis and Dr L. Dunsch for providing the molecules.

Fig.1: Schematic structure of M@C_{62} (dark circle: M atom; white circle: C atoms)