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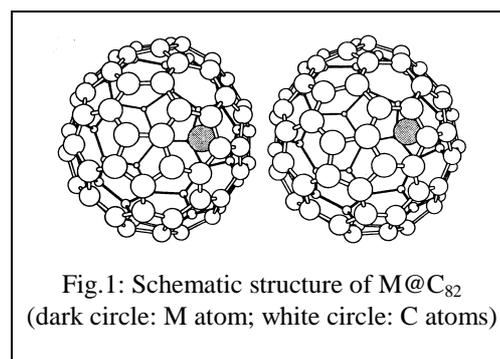
The endohedral metallofullerenes $M@C_{82}$ are unique materials in which a positively charged core metal is off-center in a negatively charged strong carbon cage (Fig.1), with promising applications such as superconductors, organic ferromagnets and laser media.[1] A strong metal-cage interaction and intrafullerene 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 $La@C_{82}$ 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.[3] 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.

In addition the magnetic ordering in these molecules is made complex by the presence of an unpaired electron spin on the $[C_{82}]^{3-}$ cage. Then any magnetic coupling could arise from metal-cage interactions or/and 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 on **the orbital contribution** of the encaged-metal magnetic moment, on the **magnetic ordering** at low temperature between the metal centers and on the **magnetic anisotropy** in $M@C_{82}$ films by using element-specific technique as X-ray magnetic circular dichroism (XMCD) in x-ray absorption (XA), in order to study the influence of the carbon cage on the RE orbital moment and therefore the large reduction of the total magnetic moment observed on the encapsulated heavy RE.

We used the superconducting magnet on ID8 beamline as high fields (up to 7T) and low temperatures (6K) were necessary. XAS and XMCD have been performed at the RE $M_{4,5}$ edges ($3d \rightarrow 4f$) on several $M@C_{82}$ ($M = Gd, Dy, Ho$), $Dy_2@C_{92}$ and $Er_2@C_{90}$ thin films. In the 18 shifts, we could prepare and measure five samples, with various coverages obtained in one shot using a wedge process. Supplementary in-house beam time (April 2003) gave us the opportunity to reproduce the results and complete the coverage dependence study with STM measurements. The molecules were supplied by Pr H. Shinohara's group in Nagoya University, Japan [4] or obtained commercially. Thin films from ~0.2ML to ~5ML were grown *in-situ* onto



Cu(111) at room temperature with a base pressure of 1×10^{-9} mbar. For this purpose, a resistively heated effusion cell, between 873 K and 930 K, has been specially designed to cope with the small quantities of material involved. The relative thickness of the films was followed by STM and using edge jumps in the XAS spectra. Every film was measured at normal ($\theta=0^\circ$) and grazing ($\theta=60^\circ$) incidence with respect to the sample surface, from 6K to room temperature. No significant in-plane // out-of-plane magnetic anisotropy has been revealed by angle dependent XMCD measurements in the films despite the “head-to-tail” molecular arrangement observed in XRD and STM studies.[5,6]

All the endohedral metallofullerene films have been first studied with XAS to probe the electronic structure of the encapsulated metal. The isotropic RE $M_{4,5}$ edges recorded at $\theta=0^\circ$ for the thickest films are shown in Fig 2(a) (open circle). The trivalent nature of the RE studied here in mono- and di-metallofullerenes has been confirmed by comparison with the calculated $3d$ x-ray absorption lines of the hole series of RE trivalent metals reported in Ref. [7] and with the respective RE_2O_3 XAS spectra.[8]

Only Dy@C₈₂ presents a slightly different line shape than Dy₂@C₉₂ and Dy₂O₃ [8] ; this discrepancy is attributed to a coverage effect. Indeed an evolution of the XAS and XMCD spectra depending on the coverage has been found in the case of Dy@C₈₂ as shown in Fig. 3. STM images are also reported in Fig. 4 following the various Dy@C₈₂ and Dy₂@C₉₂ film thicknesses. Dy@C₈₂ is first forming small clusters that are increasing progressively in size with the amount of sublimed molecules, following an island growing mode. Most of these clusters are placed on the Cu(111) terraces and few single molecules are found on the step edges. In these clusters, the molecules are supposed to arrange in a “head-to-tail” manner with a **ring-shape configuration** due to the permanent electric dipole moment along the symmetry axis of the M@C₈₂ molecules.[5,6] This is in favour of the clusters formation. Surprisingly, as long as the substrate is not completely covered by the molecules, the line shape is evolving until it reaches a bulk film line shape. This suggest either a strong interaction with Cu(111) or intermolecular interactions that cancel each other when the molecules are no more orientated due to thick coverage. On the contrary no thickness dependence has been observed on the XAS and XMCD spectra of Dy₂@C₉₂ films. Dy₂@C₉₂ films are following more a layer-by-layer growing mode, since the single molecules are covering first the step edges before to fill all the terraces at higher coverage, as can be seen on Fig.4(B). The presence of two ions inside the cage is expected to reduce the interaction with the cage, and as a result the electric dipole moment. This is in agreement with the lack of big clusters on the Cu substrate.

XMCD is routinely used to directly probe the ground state **L** and **S** (spin) magnetic moments through sum rules,[9] and to determine the element selective magnetic ordering in a composite system. Figure 2(b) shows RE $M_{4,5}$ XAS spectra recorded at a temperature of 6K with the magnetisation direction (**M**) parallel (solid line) and antiparallel (dash line) to the light direction (**P**). Except the ones from gadolinium, the circularly polarised XAS spectra are rather complicated giving rise to numerous structures in the M_5 region that are absent in the calculated spectra of the atomic trivalent ions.[10] This is related to the interaction with the carbon cage. The difference between these two XAS spectra, *i.e.* the XMCD, is displayed in Fig. 2(c). The well-known sum rules relate the intensity of the XMCD signal to the ground-state expectation value of the magnetic field operators (orbital L_z , spin S_z and magnetic dipole T_z) of the valence electrons.[9] At the RE $M_{4,5}$ edges, $\langle L_z \rangle^{4f}$ is given by $\langle L_z \rangle = -2[(\Delta A_5 + \Delta A_4) / (A_5 + A_4)] n_h^{4f}$ where n_h^{4f} represents the number of holes on the $4f$ localized orbital of the RE ion, $(\Delta A_5 + \Delta A_4)$ is the intensity of the XMCD signal integrated over a complete core-level edge and $(A_5 + A_4)$ is the unpolarized XAS spectrum integral. The second sum rule yield to the determination of the spin dependent part of the magnetic moment.[9] But in the $5d$ ions, a strong spin-orbit coupling makes $\langle T_z \rangle$ rather large and avoid it to be neglected. For this reason $\langle S_z \rangle$ will be determined by the way of atomic calculations.[*work in progress*] $\langle L_z \rangle^{4f}$ obtained by applying the sum-rules are listed in the table below. The theoretical values expected for the free RE³⁺ ions in the atomic limit are also reported for comparison.

molecules	$\langle L_z \rangle / n_h$	n_h	$\langle L_z \rangle_{exp}$	L_{th}	reduction of L	reduction of μ_{eff} [3]
Gd@C ₈₂	-0.01(2)	7	-0.1(2)	0		12.5-13 %
Dy@C ₈₂	-0.53(5)	5	-2.7 (3)	5	46 %	20.3-13.1
Dy ₂ @C ₉₂	-0.43(5)	5	-2.2(3)	5	56 %	
Ho@C ₈₂	-0.69(7)	4	-2.8(3)	6	53 %	47.6-40.3
Er ₂ @C ₉₀	-0.92(9)	3	-2.8(3)	6	53 %	33.5-26.3*

*(Er@C₈₂)

Gd@C₈₂ has been used as a reference here as Gd³⁺ is supposed to have a half filled $4f$ shell that yields zero orbital moment. Indeed the integral over $M_{4,5}$ edges returns to zero within the error bars. For the other RE ions, $\langle L_z \rangle$ is strongly reduced compared to the theoretical values

expected for a free RE^{3+} ion, from $\sim 46\%$ to $\sim 56\%$. This can not be related to a problem of magnetic saturation of the films as they were found to be magnetically saturated at $\sim 95\%$ at the working conditions of 7 T. Interestingly the μ_{eff} reduction given in Ref. [3] for the same molecules and reported in the table is lower but follow the same evolution ($\text{Gd@C}_{82} < \text{Dy@C}_{82} < \text{Er@C}_{82} < \text{Ho@C}_{82}$). One can notice by comparison between Dy@C_{82} and $\text{Dy}_2\text{@C}_{92}$ that di-metallofullerenes have lower magnetic moments than mono-metallofullerenes as expected going from atomic-like state to solid-like state. Such moment reductions have been related to a partial quenching of the orbital angular momentum of the metal due to the carbon cage crystal field and to a possible back electron transfer from the cage to the metal 5d orbitals.[3] Calculations are in progress to confirm or otherwise these hypotheses and determine $\langle S_z \rangle$.

In parallel, temperature-dependent XMCD measurements from 6K to 300K and low-temperature hysteresis loops have been investigated to determine the magnetic ordering between the entrapped metal centers. All the metallofullerenes films studied here are behaving in a similar way. The temperature dependence of the XMCD signal, from 6K to 300K and whatever the coverage, has not shown any evolution of the line shape, but only a decrease of its intensity, significative of a paramagnetic behaviour. Also the field dependence of the measured M_5 maximum dichroism at 6K showed no hysteresis loop. Only a paramagnetic coupling can be concluded from these measurements, providing no evidence of any ferromagnetic coupling between the entrapped metals as suggested by previous works.[3]

This work is the first XMCD study of these novel materials. The direct measurement of the encaged RE orbital and spin moments 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.

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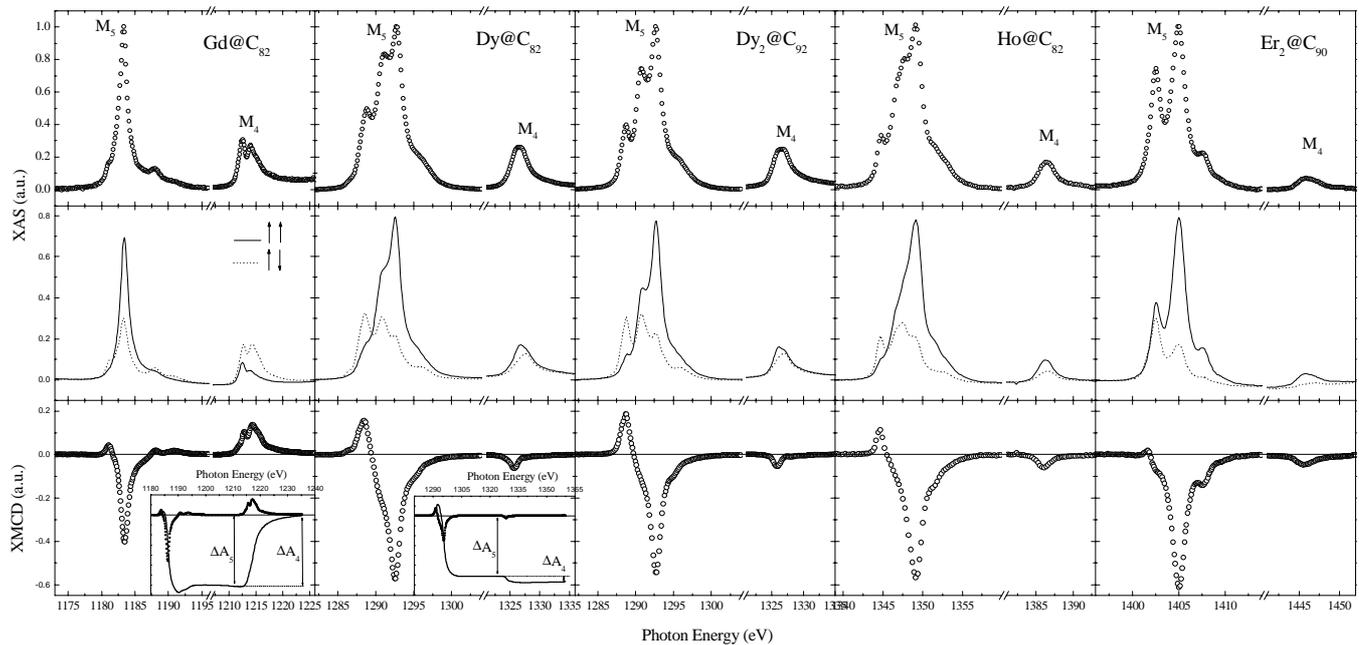


Fig.2 : (a) Isotropic RE $M_{4,5}$ XAS spectra measured at normal incidence with respect to the samples surface. The spectra are normalized to a constant edge jump. (b) RE $M_{4,5}$ XAS spectra recorded with \mathbf{M} parallel (solid line) and antiparallel (dash line) to \mathbf{P} . (c) The difference between the two spectra shown in (b) is the XMCD. In the first two panels chosen as examples, the inset shows the integral of the respective XMCD spectrum indicating the integral over the M_5 edge (ΔA_5) and the integral over the M_4 edge (ΔA_4) used to determine \mathbf{L} through sum rules.

Fig.3 : Coverage dependence of the XAS and XMCD spectra of Dy@C₈₂.

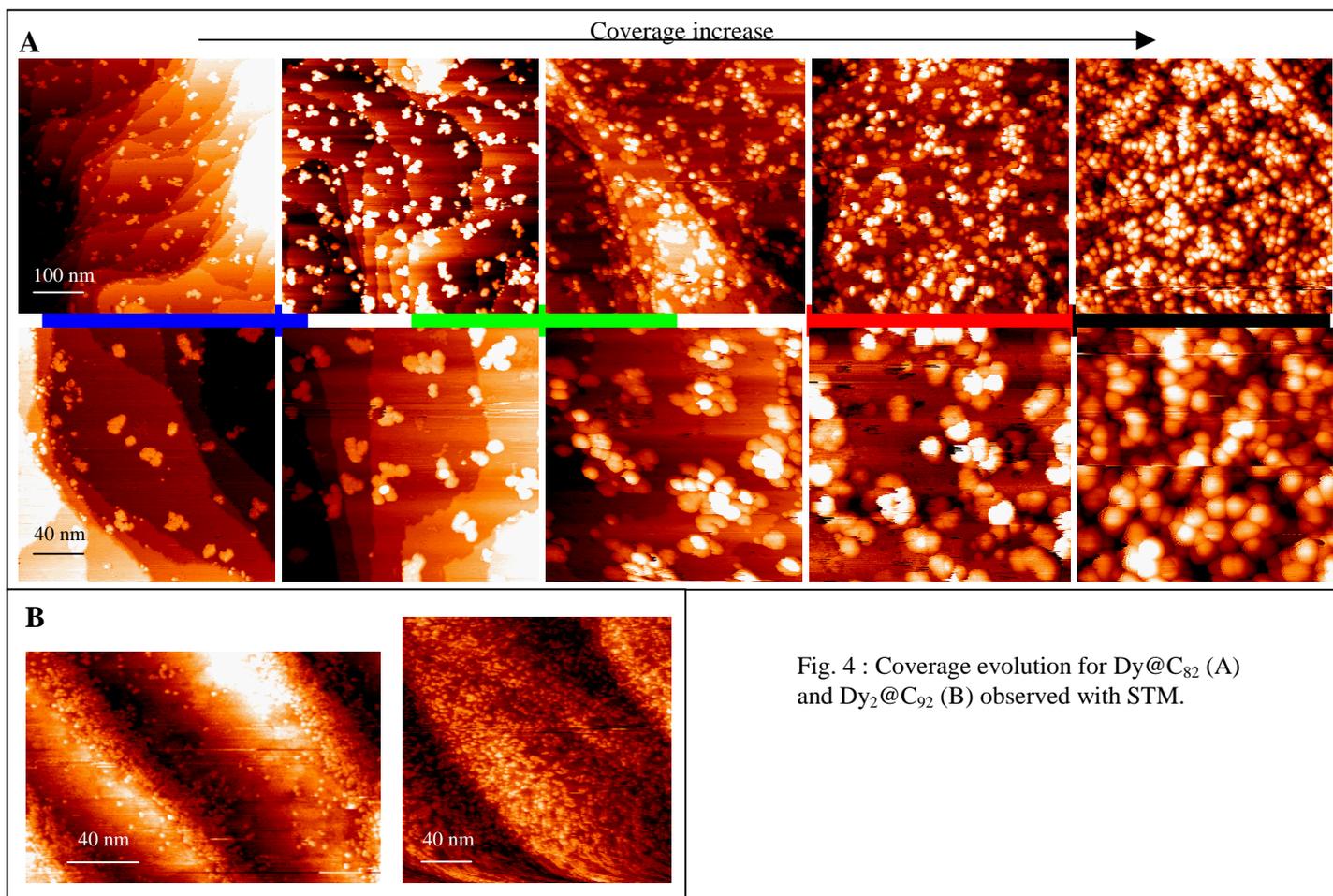
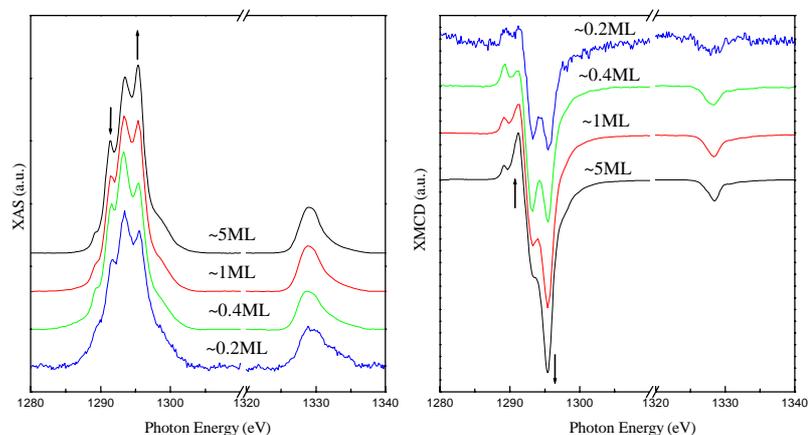


Fig. 4 : Coverage evolution for Dy@C₈₂ (A) and Dy₂@C₉₂ (B) observed with STM.

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