Study of the bimodal magnetic character of the ferromagnetic thiol capped Au nanoparticles

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We report a complete study on the magnetic behavior of ~2 nm size Au nanoparticles (NPs). These particles have been capped with the organic ligand dodecanethiol and studied by means of x-ray magnetic circular dichroism (XMCD) at BL39XU under proposal number 2009A1744. The special feature of this work lies on the ability to induce magnetic behavior on Au NPs by a simple chemical route. The magnetism of the NPs had been previously measured by SQUID magnetometry and further confirmed by XMCD under proposal number 2006B1536. Here, the former XMCD study has gone further, in fact, along with the XMCD signals at $L_{2,3}$-edges other signals were also observed at higher energies which up to date have not been analyzed. Due to the uncertainty on the origin of the magnetism of these NPs, those XMCD signals regain a high interest and so, are independently and detailed study. In addition, the confirmation of this bimodal magnetic character from same structured NPs represents an unquestionable contribution for the most basic magnetic theories.

The research towards the discovery of new properties in the field of nanoscience and nanotechnology has attracted much attention since the last decade. Among all the latest discoveries, the chemically induced magnetism in nanoparticles (NPs) of intrinsically non-magnetic elements such as Au has emerged as a promising finding. The limited quantity of metallic atoms and the large surface to bulk atoms ratio in these NPs drives an energy minimization which leads to a final electronic redistribution with electronic levels close to the Fermi one. An adequate chemical capping prevents the growing of the NPs and induces a charge transfer from surface atoms of the NPs which would also involve *d* electrons leaving these atoms virtually magnetic [1,2,3]. Macroscopically, it is observed that the magnetic signal of these NPs saturates at relatively low applied fields, suggesting collective behaviour and direct exchange coupling among the magnetic moments. Obviously, magnetic exchange coupling requires a coordinated mechanism among electrons of the whole nanoparticle, either the magnetism among the *d* unpaired electrons of the surface magnetic Au atoms is transmitted by polarization of intrinsically non-magnetic *d* electrons (inner Au atoms for instance) or directly among itinerantly characterized magnetic electrons. In any case, indirectly or directly, the magnetism must be reflected in the *d* electrons of the all metal atoms.

Here, we report the results obtained for one sample of Au NPs synthesized by a modification of the so-known Brust method [4]. In fact, when capping with thiols and under certain chemical conditions, Au NPs have happened to be ferromagnetic-like. The sample has been previously measured by SQUID magnetometer and also by x-ray magnetic circular dichroism (XMCD) (proposal number 2006B1536), and it was indeed in this former XMCD measurements that we observed that *i*) the magnetism was intrinsic to the Au atoms from the NPs and *ii*) along with the XMCD signals at $L_{3,2}$-edges of an order of magnitude of 10^{-5} of the XAS step height, other different signals were clearly observed (Fig. 1).

The just mentioned former XMCD results have been the motivation to carry out the present experiment. Here again, the study has been performed at the Au $L_{2,3}$-edges (113734 eV and 11919 eV respectively) at the BL39XU beamline at room temperature (RT) and at 2 K. The detection of the XMCD spectra was done in the transmission mode under an applied magnetic field of 10 T and, samples were spread and stuck onto a Kapton tape.

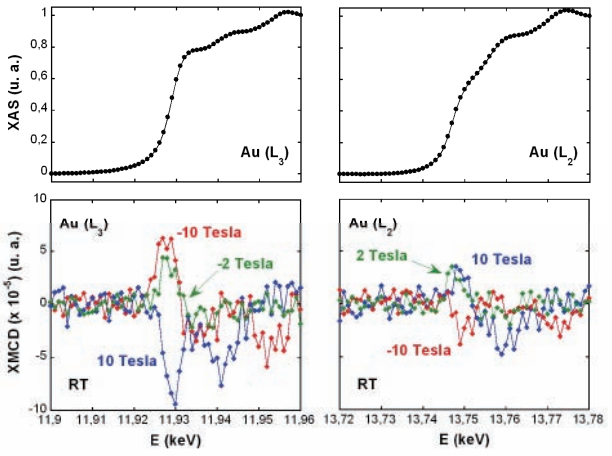

Figure 1. XMCD and XAS spectra obtained at the Au L_3 and L_2 edge with applied magnetic field of 10 T and 2 T at RT. XMCD spectra have been normalized taking into account a branching ratio of 2:1 in the dipole transition for L_3 and L_2 edges.

In Figure 1 the XMCD signals at $L_{3,2}$-edges along with the just mentioned other signals can be observed. These signals have also a magnetic nature, confirming the involving of complementary *d* electrons in the magnetism of the NPs. The evolution all XMCD signals has been independently analyzed both at RT and at 2 K (Fig. 2). The element specific magnetization (ESM) of the signal at the L_3-edge energy shows clearly a ferromagnetic character and hysteresis behaviour even at RT. Nevertheless, the analysis of the XMCD signals at higher energies shows a completely different magnetic character. At these last energies, 11.931 keV and 11944 keV respectively, ESM measurements evolve linearly with the applied magnetic field being the slope independent to the temperature. Note that a lineal and temperature independent evolution of the magnetic signal is characteristic of magnetic signals governed by Pauli's paramagnetism. The sign of the slopes are different for the ESM of the different structures which could evidence an antiferromagnetic exchange coupling among the *d* electrons involved.

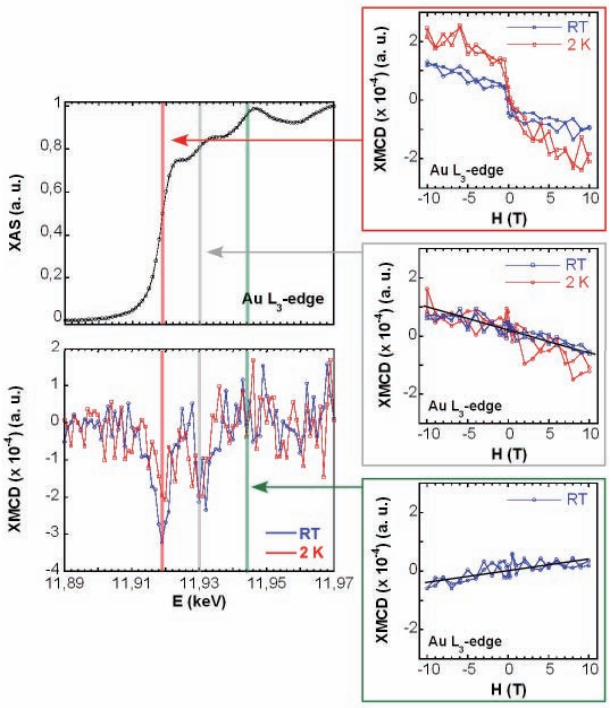

Figure 2. XMCD and XAS spectra obtained at the Au L_3 edge with applied magnetic field of 10 T at RT and 2 K along with the ESM measurements performed at both temperatures at the three different signals observed.

In conclusion, we have demonstrated that thiol capped ferromagnetic Au NPs present a double magnetic behaviour. These different magnetic behaviours are located on magnetically independent *d* electrons with energy above the Fermi level. The confirmation of this bimodal magnetic character from same structured NPs represents an unquestionable contribution for the study and characterization of the charge transfer magnetic anisotropy which supports this novel magnetism.

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