XMCD measurements on thiol capped gold and silver nanoparticles.

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The aim of the here reported experiment was the element selective observation of magnetization of Au nanoparticles. We performed a hard x-ray magnetic circular dichroism (XMCD) study at the Au $L_{,2,3}$ -edges on the Au-SC_nH_m systems. The signals observed at Au $L_{,2,3}$ -edges, together with the hysteresis loop measured at L_{3} -edge corroborates the intrinsic ferromagnetic behavior of the Au nanoparticles. Up to now, this is the first time that has been proved the nature of the magnetic behaviour in these nanoparticles.

Since the appearance of magnetism in thiol capped Au nanoparticles [1, 2], characterized by magnetic hysteresis up to room temperature, some questions have been launched in order to find the origin of ferromagnetism. We have followed the procedure proposed in Ref. [1] to synthesize these Au magnetic nanoparticles obtaining similar magnetic responses than those published in Ref [1].

Experiments were performed using the highly sensitive spectrometer installed al BL39XU of SPring-8 synchrotron in the 5 – 20KeV energy range, being only possible to record the XMCD signal at the Au L_{2,3}-edges. Detection of XMCD spectra was done in the transmission mode. Six different powder samples were uniformly spread between two kapton layers: 8 mm long x 4 mm wide x 0.5 mm thick (Au_001, Au_002, Au_003, Au_004, Au_005, Au_006). As the signal was very low, for every sample different quantity of layers were combined in order to improve the signal. Firstly, X-ray absorption spectroscopy (XAS) and XMCD spectra for all the samples were performed at L3 edge ($2p3/2 \rightarrow 5d5/2$, 6s1/2 dipole allowed transitions) at room temperature in applied magnetic fields of 5T and 10T. The XMCD amplitude was of the order of 10^{-4} of the XAS step height. After the first checking of the XMCD signal of the samples, we centered the study on the Au_002 sample. Figure 1 shows the XMCD signals obtained from the selected



Fig. 1 XMCD spectra at the Au L₃-edge with an applied magnetic field of 10T.

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Au002 sample at L3 edge (11.93 keV) for a external applied field of \pm 10 Tesla.

The appearance of XMCD reversed signals, when the magnetic field direction changes, for the different samples corroborates that the observed signal is certainly of magnetic origin and does not arise from any impurity. Small positive peak structures were observed at the high-energy side of the main peak, at around 11.94 and 11.955 keV, which could be attributed to the paramagnetic signal form bulk atoms.

In order to improve the signal/noise ratio certain quantity of scans using the same procedure and parameters were performed on the sample. XMCD spectra of Au002 sample were also recorded at the L_2 -edge ($2p_{1/2} \rightarrow 5d_{3/2}$, $6s_{1/2}$) at R.T. in an applied magnetic field of 10T (Fig. 2). A negative signal was also observed at the L_2 -edge (13.75 keV), together with small peaks at 13.76 and 13.77 keV.

Finally, as the XMCD signal is proportional to the magnetization, element specific magnetization (ESM) was obtained by recording the peak amplitude of the XMCD spectra at the Au L_3 -edge as a function of the external magnetic field. Fig. 3 shows the ESM



Fig. 3. XMCD peak intensity of Au-SR sample, as a function of applying magnetic field at Au L₃-edge.

measurements up to 2T for the Au002 sample. ESM increases with increasing magnetic field reaching saturation and follows a hysteretic behavior as the applied field decreases, similar to that obtained in the M vs H SQUID magnetization measurements. In this way, ferromagnetic intrinsic behavior of Au-SR nanoparticles has been proved by these specific XMCD measurements.

[1] P. Crespo et al., Phys. Rev. Lett. 93 (2004) 087204.
[2] Y. Yamamoto et al., Phys. Rev. Lett. 93 (2004) 116801.



Fig. 2 XMCD spectra at the Au L₂-edge with an applied magnetic field of 10T.