

Study on the relation between local surface structure and induced magnetism on thiol-capped Au nanoparticles with different magnetic characters by means of XMCD measurements

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We report a study on the magnetic behavior of various ~2 nm size Au nanoparticles. These particles have been capped with thiol type organic ligands and studied by means of magnetic circular dichroism (XMCD) at BL39XU under proposal number 2008A1701. The samples under study present different magnetic characters induced by varying the concentration of the initial metallic salt precursor. Here, the results obtained by means of 'classical' magnetic measurements have been compared with those obtained by the X-ray absorption technique with the purpose of getting more information on the possible physical mechanism responsible for the magnetism of organically capped metallic nanoparticles.

Ever since the discovery of magnetic Au nanoparticles many research groups from very different backgrounds have directed their efforts toward the synthesis of this kind of systems. After all, this topic combines both scientific interest and potential applicability. Up to now various results have been published dealing with organically capped magnetic Au nanoparticles. However, from one work to other, even if regarding particle size there is a good agreement among all, the magnetism of the samples varies and the hypotheses around the physical mechanisms responsible for the magnetic properties seem not to be conclusive so far. It is patent that nanoparticles must have high magnetic anisotropy, but discrepancies arise when it comes to associate this anisotropy to a high orbital contribution. For instance, not only for the case of Au nanoparticles synthesized by our group, but also for thiol-capped Ag and Cu counterparts we found that the magnetic signal saturates even at room temperature and under moderate applied fields, indicating collectivity between the magnetic moments of the surface metal atoms. The origin of

this collective state was thought to be due to the coupling exchange among the spins of the located d electrons responsible for the magnetism in the samples. In fact, by means of XMCD spectroscopy, $\langle \mu_L / \mu_S \rangle$ was calculated to be 0.10 for a sample labelled Au002, not a sufficiently great value if one wants to point orbital contribution as a determinative factor. Besides, we have also observed differences in the magnetization and remanent field values of various thiol-capped magnetic Au NPs even if the chemical synthetic route followed was similar. This fact let us think that during the synthesis small environmental variations could lead to small differences in size, morphology and in the electronic redistribution, and consequently, in the magnetic response as well.

In order to clarify and shed light on this topic, here we report the results obtained by means of XMCD for two samples of thiol-capped Au nanoparticles. Then, we will compare those results with the formerly mentioned sample Au002. All three samples have been synthesized by a modification of the so-known Brust method, varying the initial

[Au³⁺]. The two samples selected for this experiment, Au4dt250(3) and Au3dt250(7), were chosen owing to their magnetization values, which were measured by VSM (Vibrating Sample Magnetometer) (Fig. 1).

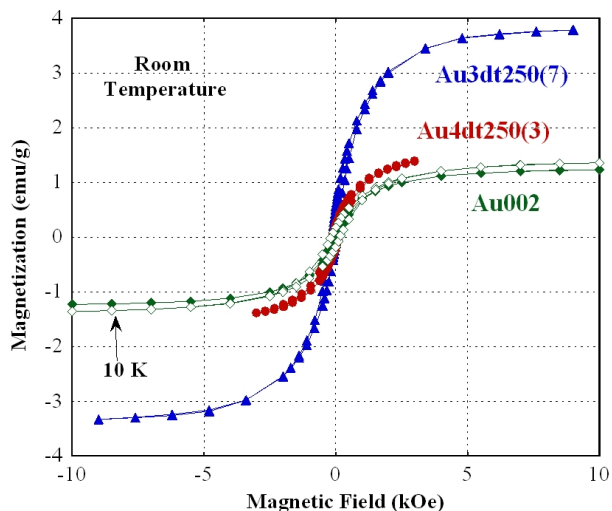


Figure 1. VSM measurements of samples Au4dt250(3) and Au3dt250(7) at room temperature. The hysteresis loops of those samples are compared with that of sample Au002. Notice that this sample was measured with a SQUID magnetometer at room temperature and at 10 K.

X-ray absorption measurements were performed using the highly sensitive spectrometer installed at BL39XU of SPring8. Detection of XMCD spectra was done in the transmission mode under an applied magnetic field of ~ 2 T and, sample preparation was done by spreading the nanoparticles between two polyimide films. XAS and XMCD spectra were performed at Au L₃-edge, at 11.919 keV ($2p_{3/2} \rightarrow 5d_{5/2}, 6s_{1/2}$ dipole allowed transitions), being the XMCD amplitude of the order of 10^{-5} of the XAS step height. Figure 2 shows the XMCD signals obtained from the selected Au3dt250(7) and Au4dt250(3) samples, together with the previously measured Au002 sample. According to the magnetization measurements, one should expect to have the greatest XMCD signal for sample Au3dt250(7), then for sample Au4dt250(3) and finally for Au002. However, this theoretical order is

reversed in the experimental results, and leaves the doors open to think that it might be possible that in addition to d electrons, also electrons from another shells could be involved in the magnetic response.

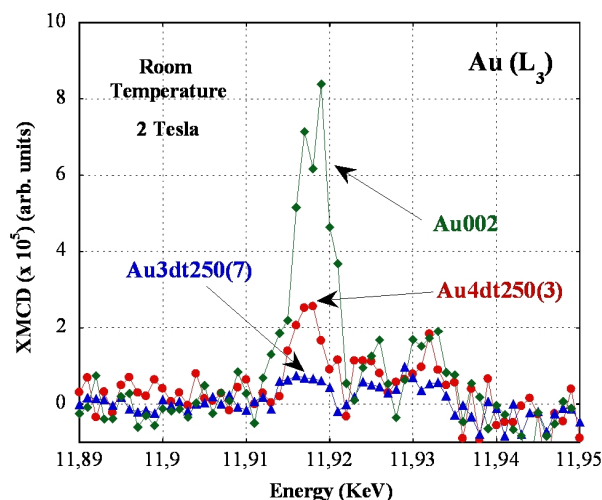


Figure 2. XMCD measurements of samples Au4dt250(3), Au3dt250(7) and Au002 at room temperature.

To conclude the experiment, element specific magnetization (ESM) measurements were obtained by recording the peak amplitude of the XMCD spectra at the Au L₃-edge as a function of the external magnetic field up to 2T. In Figure 3 the hysteretic behaviour can be observed for both samples, although the saturation values are smaller than those observed for the previously measured Au002 sample, just as it could be expected after XMCD measurements.

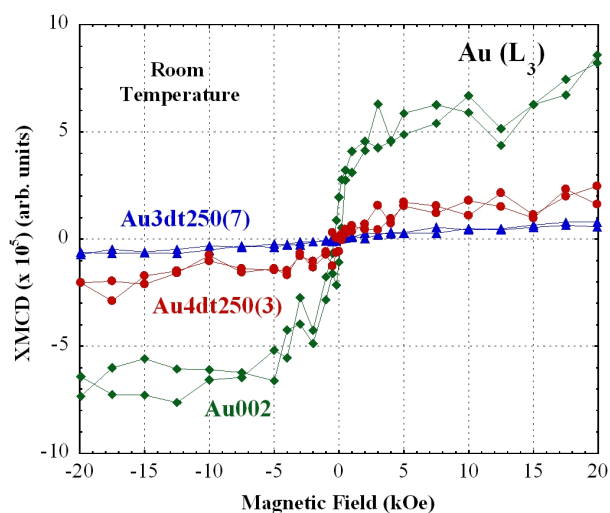


Figure 3. ESM measurements of samples Au4dt250(3), Au3dt250(7) and Au002 at room temperature.