

Magnetism of noble metal nanoparticles: a XAS and XMCD study

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The understanding of the magnetic properties and electronic structure of nanoscopic systems is a very important goal of today nanoscience. In particular, the onset of magnetic moment in nanosized particles of metals which are non magnetic in its bulk form has attracted interest recently. We have synthesized Au nanoparticles (NPs) with diameters of few nm on a biological template, a protein S-layer of *Sulfolobus Acidocaldarius* bacteria, and Pt nanoparticles on the cages of NaY zeolite [1]. The magnetic properties of the particles have been characterized by means of SQUID magnetization as well as X-ray absorption (XANES and EXAFS) and magnetic circular dichroism (XMCD) spectroscopies.

Magnetization data taken at $1.8 \text{ K} < T < 300 \text{ K}$ and $0 < B < 7 \text{ T}$ reveal a clear superparamagnetic behavior of these materials. The magnetization arises from the Pt and Au NPs as it has been proven by XMCD spectroscopy at the Pt and Au $L_{2,3}$ -edges performed at low temperatures. From the XAS measurements the number of holes n_h in the 5d band of these systems is found. Au-S bonds have been also detected by XANES measurements at the S K-edge. Besides, by means of EXAFS analysis at the Pt and Au L_3 -edge, the internal crystal structure of the NPs is characterized as Pt_{13} in one case, and fcc gold in the other, with Au-S bonds located at the particle surface. In both cases, the magnetism of NPs is correlated to an increase of the hole charge carrier density in the metal 5d band caused by the exchange of electrons with the supporting media.

The average total, orbital and spin momenta per metal atom have been determined from XMCD by the application of sum rules: $\mu/\text{Pt atom} = 0.28(1)\mu_B$ and $\mu/\text{Au atom} = 0.050(1)\mu_B$, respectively, with a ratio $m_L/m_S \approx 0.30$ for Pt and $m_L/m_S = 0.29$ for Au. The fit of the XMCD field dependence to a Langevin function is a very powerful tool, yielding the total magnetic moment per particle ($\mu_{\text{total}} = 3.7 \mu_B$ for Pt and $2.3 \mu_B$ for Au), and a *magnetic-only* determination of the size of the particle. The observed magnetic moment per Au atom is 25 times larger than those previously found by XMCD in Au-thiol capped NPs.

Our results illustrate the significance of the extension of the recent experimental capabilities of the ID12 beamline to lower temperatures (in the range $2.2 < T < 10 \text{ K}$) and to higher magnetic fields, up to 17 T.

References

[1] J. Bartolomé et al., Phys. Rev. B **80**, 014404, (2009).