



	Experiment title: XAS study on nanoparticles system	Experiment number: 25-01-622
Beamline: BM25	Date of experiment: from: 03-05-06 to: 09-05-06	Date of report: 14-12-06
Shifts: 18	Local contact(s): Juan Rubio Zuazo	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): M ^a Luisa Fdez-Gubieda J.S. Garitaonaindia M ^a Angeles Laguna Marco Eider Goikolea		

Report:

The studies performed in a wide variety of inorganic nanoparticles with discrete compositions and sizes indicate that their properties are not only affected by size and shape but also by their surface composition, specific spatial ordering, and interactions with surrounding media. In the case of thiol-capped gold nanoparticles, the report of ferromagnetism at room temperature [1] has gained interest because of the practical applications related to this behaviour. The appearance of ferromagnetism in these nanoparticles of 1.4 nm seems to be totally linked to the chemical route selected for their synthesis, where the ligands and surfactants chosen as protective agents would play a crucial role. So, according to Crespo *et al.*, and mainly based on EXAFS data, when Au nanoparticles are stabilized with thiol capping-ligands 5d localized holes would be created by the Au-S bonds. The ferromagnetism would be mediated by the large surface to volume ratio, rather than the small size of the nanoparticles and, so, this would be totally localized on the surface. Besides that and to add more importance to the Au-S bond, the value of the magnetic moment would be completely dependent to the electronic transference between the surface Au atom and the S ligand [2]. Recently, we have discovered that following a similar chemical route, ferromagnetic Ag nanoparticles can also be synthesized.

XAS measurements were performed in order to characterize thiol capped Au, Ag and Cu nanoparticles. The data were collected at BM25 (SPLINE) beamline working at room temperature. Many different samples (including the metal foils used as references) were studied, varying the metal/thiol ratio from one to another. During the available beamtime we were able to perform a complete experiment on Au at the Au L₃-edge 11.92 keV, on Ag at the Ag K-edge 25.51 keV and on Cu K-edge 8.98 keV. Moreover, we always collected data at least 3 times per edge in order to be able to statistically analyze it. The

normalized XANES spectra of thiol capped Au and Ag nanoparticles showed the same resonance pattern as that of bulk metal with a significant broadening, indicating that they have a metal-like environment but with a significant disorder. In good agreement with the results of Crespo *et al.*, it can also be observed in the case of Au how the whiteline intensity increases from bulk to nanosized samples, indicating a possible increase in d-hole population just above the Fermi-level. However, in the case of Ag nanoparticles the whiteline does not show such an evident intensity increase, which can call into question the interpretation about the origin of the ferromagnetism. In the case of Cu, a deeper study must be carried out because as it can be seen from the spectra, the sample has a metal and oxide-like environment.

Finally, we would like to thank the SPline team for competent support and help all through our experiments and before and after our arrival to the ESRF, as well as the personnel at the facility for their assist in all the aspects of their competence.

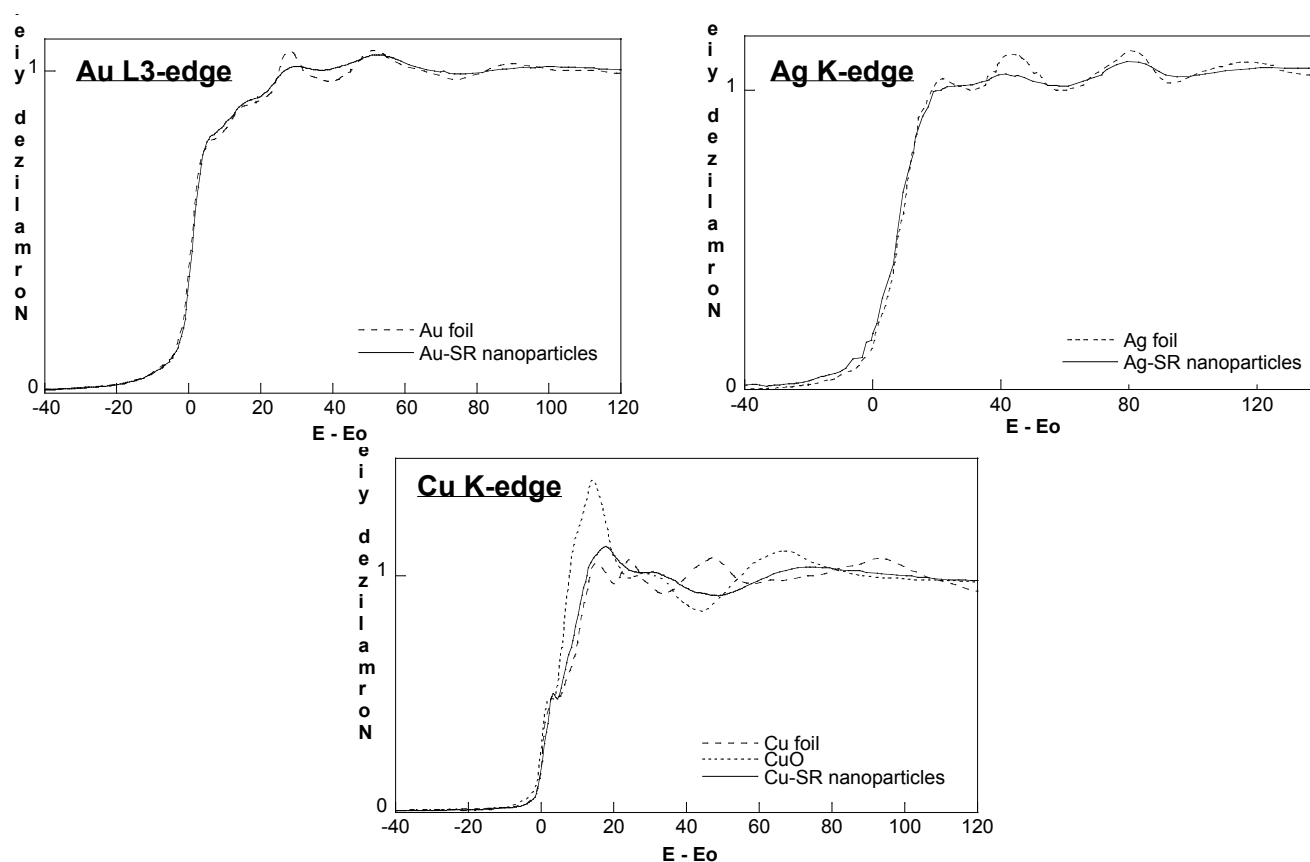


Figure 1. Au L3-edge, Ag K-edge and Cu K-edge XANES spectra of the NP samples and references (metal foils and CuO).

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