

Ferromagnetic Resonance in Amine/Organic Acid Caped Au-Nanoparticles Assisted by Yttrium-Oxide

G. G. Lesseux^{*}, W. Iwamoto^{*}, V. H. Rosas^{**}, C. Vautier-Giongo^{**}, D. Rettori^{**}, R. R. Urbano^{*}, and C. Rettori^{*,***}

^{*}Instituto de Física "Gleb Wataghin", UNICAMP, Campinas-SP, 13083-859, Brazil, lesseuxgg@gmail.com, iwamoto@ifi.unicamp.br, urbano@ifi.unicamp.br

^{**}Lab. de Química e Bioquímica de Espécies Altamente Reativas, UNIFESP, Diadema-SP, 09972-270, Brazil, carolinavtgiongo@gmail.com, danielrettori@hotmail.com, v.hrosas@hotmail.com

^{***}Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Santo André, SP, 09210-170, Brazil, rettori@ifi.unicamp.br

ABSTRACT

In this study we report on the magnetic properties of amine/organic acid caped Au-nanoparticles (Au-NPs) assisted by yttrium-oxide (Y_2O_3) with diameters ranging between 20 and 60 nm, prepared by somewhat modified chemical route already described in the literature. The magnetization results show a ferromagnetic (FM) loop with negligible coercive field and a magnetic saturation of ~ 0.1 emu/gAu at 2 K. Furthermore, an intense magnetic resonance was observed from room- T down to 4.2 K with the following features: *i*) the field for resonance, H_R , is sample and weakly T -dependent; *ii*) the line width, ΔH_{PP} , broadens at low- T ; and *iii*) the resonance intensity remains almost constant in the entire T -region. The observed resonance is the signature of a ferromagnetic resonance (FMR). To the best of our knowledge this is the first clear report on FMR in magnetic caped Au-NPs. These features characterize our Au-NPs as FM ones. Our results are discussed in terms of the interactions established between the capping ligands and the surface of the Au-NPs which stimulate an effective hybridization of the $5d$ - $6s$ conduction electrons of the Au atoms, allowing the Au $5d$ shell to become magnetic due to uncompensated $5d$ spins.

Keywords: Ferromagnetic Resonance, Au nanoparticles, ESR.

1. INTRODUCTION

The study of metallic nanoparticles (NPs) is today a subject of deep concern among the scientific community of physicists, chemists, and engineers due to their broad applications in high density storage media,[1] catalysis,[2] sensors devices,[3] and also for the basic underlying physics involved,[4] which is usually quite different than that of the corresponding bulk material.[5,6] The two important controlling factors which determine the properties of the nanometric materials are: *i*) the "size effect", when the electron confinement become comparable to the wavelength of the electrons at the Fermi level, and *ii*) the "surface effect", due to the presence of a relative large number of

atoms at the surface with different chemical bonds and structural topology. These two effects certainly influence the total energy and also control the final structure and shape of the NPs. Since most of the Au atoms are on the surface of the NPs, they are responsible for the total energy and stabilization of the system.[7,8] Therefore, the charge distribution on the NPs may be different from that of the bulk surface due to the electrons quantum confinement.[9,10]

The surprising discovery that gold-nanoparticles (Au-NPs) display magnetic properties in contrast to the diamagnetic behavior of the bulk material has stimulated several studies aimed to understand this phenomenon.[11] Actually, magnetic nanoparticles are of great interest in data storage and in health science fields. In this communication we report on the ferromagnetism (FM) and the Ferromagnetic Resonance (FMR) between room- T and 2 K of yttrium-oxide (Y_2O_3) assisted amine/organic acid caped Au-NPs of diameters ranging between 20 and 60 nm. The results are discussed in terms of the interactions established between the capping ligands and the surface of the Au-NPs.

2. EXPERIMENTAL DETAILS

2.1. Samples preparation

Two samples (namely, S1 and S2) of Y_2O_3 assisted amine/organic acid caped Au-NPs, with diameters ranging between 20 and 60 nm, were prepared by an adapted chemical method taken from the literature. [6, 12, 13] The process consisted in the preparation of two precursor compounds. Precursor 1 was obtained by dissolving 0.41 mmol of $HAuCl_4 \cdot 3H_2O$ and stoichiometric excess of triphenylphosphine (PPh_3) in 40 mL of acetonitrile. This solution was heated up to 80 °C until the evaporation of the solvent was completed. Needle type crystals of $AuCl(PPh_3)$ were obtained in this stage. Precursor 2 was prepared by heating fine powder of Y_2O_3 (0.02 mmol) and trifluoroacetic acid (6 mL), under argon flow until the evaporation of trifluoroacetic acid was also completed. Then, precursor 1 was dissolved in benzyl ether (20 mL) together with oleylamine (6 mL), oleic acid (6 mL), and precursor 2 was added to this

mixture. The complete system was heated up to 100 °C with vigorous stirring under an argon flow for 20 minutes to allow all the water to be evaporated. Thereafter, heating was increased to 200 °C under reflux and 2 mL of a 1 M THF solution of lithium triethylborohydrate reductor was added to the solution. The temperature was then increased to 250 °C for 20 minutes under argon flow. Finally, the solution was cooled down to room- T and centrifuged after adding excess of ethanol. The nanoparticles can be easily dispersed in non-polar solvents such as toluene. We should mention that several other samples were prepared following the same recipe leading to results similar to those of sample S1. Moreover, few samples using Er_2O_3 , instead of Y_2O_3 , were prepared and the results were similar to those of sample S2 but with somewhat enhanced magnetic behavior due to the intrinsic Er^{3+} ($4f^{11}$) magnetic moment. Furthermore, as a reference a third sample, S3, was also prepared but skipping the stage with precursor 2. All used reagents were non-magnetic high purity grade purchased from Sigma-Aldrich and tested to be free of magnetic impurities by magnetization and ESR measurements.

2.2 Experimental techniques

The size and shape of the two samples were analyzed in a HRTEM (JEM 3010, 300 keV microscopy) and the structure by X-ray powder diffraction in a $\text{Cu-K}\alpha$ radiation in a Phillips diffractometer at room- T . The magnetic properties were characterized by means of magnetization measurements as a function of the magnetic field, H , up to 5 Tesla and temperature, T , between 300 K and 2 K using a superconducting quantum interference device (SQUID) magnetometer MPMS-5 (Quantum Design). For the Ferromagnetic Resonance (FMR) experiments between 4.2 K and 300 K, we used a Bruker ELEXYS X-Band (9.5 GHz) spectrometer with a T_{102} resonator coupled to a cool helium gas flux cryostat and an Oxford T -controller.

3. EXPERIMENTAL RESULTS

3.1. Structure characterization

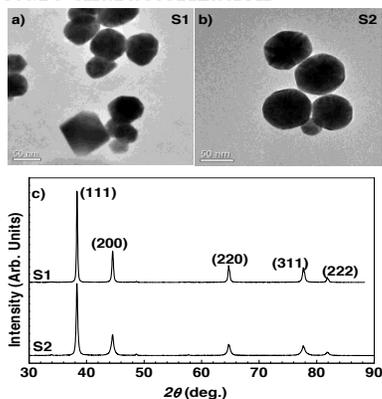


Figure 1: S1 and S2 Au-NPs assisted by Y_2O_3 synthesized at 260 °C in Oleylamine/Oleic Acid solution: a) and b) HRTEM microimages; c) X-ray powder diffraction patterns.

Figures 1a and 1b present the TEM (HRTEM) microimages for the S1 and S2 samples, respectively. These microimages show that the shapes of the NPs are not regular with a rather large size distribution going from 20 nm to 60 nm. Figure 1c presents the X-ray powder diffraction patterns for samples S1 and S2 which were indexed on the basis of the face-centered-cubic (fcc) Au powder diffraction data.

3.2. Magnetization Experiments

Figure 2 presents the magnetization measurements (M vs H) at 2 and 300 K for the S1 and S2 samples. From the saturation magnetization at 2 K we have estimated $\sim 3 \times 10^{-3} \mu_B/\text{Au}$ for S1 and S2. Differently from other reports [14] and within the accuracy of our experiments, no hysteresis loop was observed in any of these samples. The main difference between S1 and S2 is the sizable magnetic saturation of $\sim 1.5 \times 10^{-3} \mu_B/\text{Au}$ observed at 300 K for S2. The M vs H data for the reference S3 sample at 2 and 300 K only showed the diamagnetism of the Au-NPs (not shown).

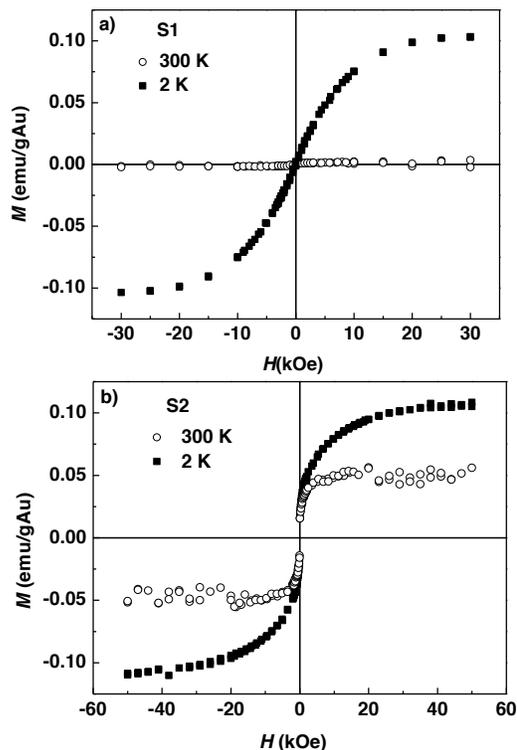


Figure 2: M vs H at 2 K and 300 K for: a) S1 and b) S2 samples. The diamagnetism contribution was subtracted in all data.

Figure 3 presents the T -dependence of the zero field cooling (ZFC) and field cooling (FC) magnetization (M vs T) at $H = 200$ Oe between 2 and 300 K for S1 and S2. We believe that the temperature where the magnetization becomes reversible, T_R , ~ 256 K and ~ 50 K for S2 and S1, respectively, is associated with clusters of interacting magnetic Au-NPs imbedded in the residual supporting

emulsion, other than the blocking temperature, T_B , of the superparamagnetic Au-NPs.[15]

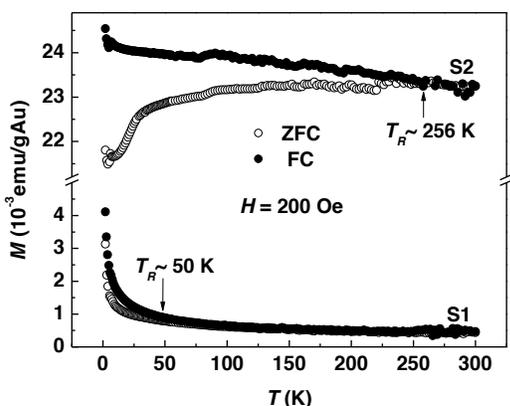


Figure 3: T -dependence of the ZFC and FC magnetization at $H = 200$ Oe between 2 K and 300 K for the S1 and S2 samples.

3.3. ESR Experiments

Figure 4a shows the X-band ESR spectra at room- T , 100 K and 8 K for S1. Figure 4b presents the X-band ESR spectra for S2 at different temperatures following the *in-situ* ESR thermal treatment: the “as prepared” sample at room- T ; then at 95 K, after cooling; then at 370 K, after heating; and at room- T again, after cooling. It is clear from these data that the observed *lineshape* and *structure* of the ESR spectra has dramatically changed during this thermal cycling.

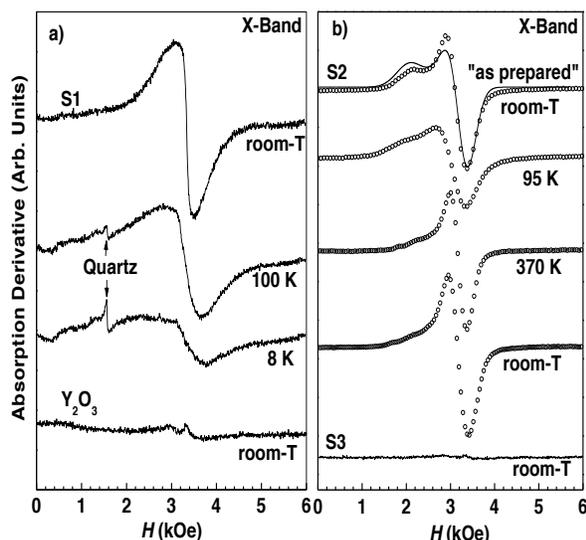


Figure 4: T -dependence of the X-band ESR spectra for: a) S1 sample; b) S2 sample. The ESR spectra for the Y_2O_3 powder and S3 at room- T are shown in a) and b), respectively, for comparison. The solid line on the ESR spectra of the “as prepared” S2 sample corresponds to a simulation of the powder spectrum (see text).

The solid line in Figure 4b on the spectrum of the “as prepared” sample is a simulation of the powder spectrum for a random distribution of resonances with g_{\perp} and g_{\parallel} which correspond to a demagnetization field of $H_D \approx 780$ Oe along the shortest dimension of the NPs. This demagnetization field disappears almost completely after the thermal cycling. This is strong evidence that the distribution of the magnetic Au-NPs has been rearranged in the presence of the external magnetic field ($H \approx 3.4$ kOe) as a consequence of the mobility and facility of the NPs to reorienting in the viscous media where they are imbibed.

A comparison between the ESR intensities of the S1 and S2 samples yields to a factor of $I_{S2}/I_{S1} \approx 25$. It is worth mentioning that no ESR signal was observed for S3 and for the used Y_2O_3 compound at all measured temperatures (see their room- T *silent* spectra in Fig. 4a,b). The single ESR line observed at 1.5 kOe is a background signal due to Fe^{2+} impurities, typically present in some of our quartz sample tubes.

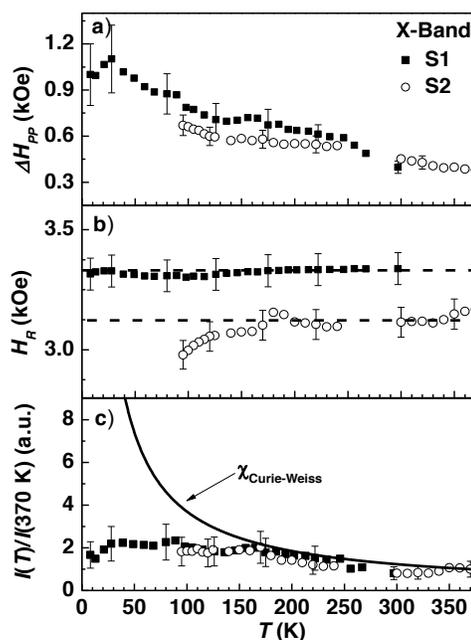


Figure 5: T -dependence of the ESR parameters extracted from the observed spectra of the S1 and S2 samples: a) peak-to-peak line-width (ΔH_{PP}); b) field for resonance, (H_R); and c) relative intensity $I(T)/I(370$ K). The solid line is the Curie-Weiss susceptibility behavior.

Figure 5 presents the T -dependence of the ESR parameters extracted from the observed spectra of both S1 and S2. These data show that the peak-to-peak line-width, ΔH_{PP} , broadens, the field for resonance, H_R , is sample and weakly T -dependent and the relative intensity, $I(T)/I(370$ K), does not follow a Curie-Weiss behavior at low- T . These features are the characteristic signature of a ferromagnetic resonance (FMR). [15] The lower

resonance field, H_R , its weak low- T dependence and the stronger ESR intensity of S2 compared to S1, are probably associated with the stronger low field magnetization, $M(H < 5 \text{ KOe})$, found for S2 (see Figs. 2 and 3). Then, the different H_R for S1 and S2 should be associated with a stronger demagnetizing field of the S2 sample. Therefore, we argue that the amine/organic acid capped Au-NPs assisted by Y_2O_3 is a new and promising route for the production of magnetic Au-NPs.

4. ANALYSIS AND DISCUSSION

Nowadays it is a consensus that the magnetism in metallic capped Au-NPs is associated with the so-called “*Fermi hole effect*”[16] or “*ligand effect*”, where $5d$ localized holes are generated by the Au-X bonds on the surface of the NPs, where X is a highly oxidative element like S,[14] P and Cl.[17] These holes may give rise to localized magnetic moments with high spin-orbit coupling (1.5 eV) for gold in a local low symmetry due to the Au-Au and Au-X bonding.[18] Although the “*size effect*” tends to decrease the number of holes,[19] it has been argued that the “*ligand effect*” may counter balance the “*size effect*” and thus the capped Au-NPs may exhibit an observable magnetism. [20, 21, 22] The Y_2O_3 assisted amine/organic acid capped Au-NPs studied in this work present a saturated magnetic signal and a FMR between room- T and 2 K, indicating the existence of a magnetic collective state for the coupled magnetic moments. The origin of this collective state is probably caused by the exchange coupling between the spins of the localized Au- $5d$ holes which are responsible for the FM in these Au-NPs.

In summary, our work in Y_2O_3 assisted amine/organic acid capped Au-NPs has demonstrated that: *i*) the magnetic properties of these Au-NPs can also be observed via a FMR experiment; *ii*) via the FMR it is possible to show the existence of *demagnetizing NP shape effects* in the magnetic Au-NPs; and *iii*) the Y_2O_3 assisted chemical route is an efficient alternative method for the production of an enhanced magnetism in capped Au-NPs via, presumably, additional surface Au-O bonds.

ACKNOWLEDGMENT

The TEM data was acquired in the LME/LNNano at the Brazilian Synchrotron Light Laboratory (LNLS). The high- T ESR data were taken at the CEM of the Universidade Federal do ABC, Brazil. The authors thank FAPESP (SP-Brazil), CNPq and CAPES (Brazil), for supporting this work.

REFERENCES

[1] S. Sun, C. B. Murray, D. Weller, L. Folks, and A. Moser, *Science*, 287, 1989, 2000.
 [2] B. F. G. Johnson, *Top. Catal.*, 24, 147, 2003.
 [3] X. Luo, A. Morrin, A. J. Killard, and M. R. Smyth, *Electroanalysis*, 18, 319, 2006.

[4] Y. Volokitin, L. J. Sinzig, J. G. de Jongh, G. Schmidt, M. N. Varafik, and I. I. Moiseev, *Nature*, 384, 621, 1996.
 [5] R. F. Service, *Science*, 271, 920, 1996.
 [6] G. Schmid, and B. Corain, *Eur. J. Inorg. Chem*, 17, 3081, 2003.
 [7] K. Nobusada, *J. Phys. Chem. B*, 108, 11904, 2004.
 [8] H. Liu, B. S. Mun, G. Thomson, S. R. Isaacs, Y. S. Shon, D. F. Ogletree, and M. Salmeron, *Phys. Rev. B*, 72, 155430, 2005.
 [9] P. Zhang, T. K. Sham, *Phys. Rev. Lett.*, 90, 245502, 2003.
 [10] C. López-Cartes, T. C. Rojas, R. Litrán, D. Martínez-Martínez, J. M. de la Fuente, S. Penades, and A. Fernandez, *J. Phys. Chem. B*, 109, 8761, 2005.
 [11] A. Roldán, F. Illas, P. Tarakeswar, and V. Mujica, *J. Phys. Chem. Lett.*, 12, 2996, 2011.
 [12] J. M. Vargas, W. Iwamoto, L. M. Holanda, Jr., S. B. Oseroff, P. G. Pagliuso, and C. Rettori, *J. Nanosci. Nanotechnol.* 11, 2126, 2011.
 [13] Y. Tang and M. Ouyang, *Nature Materials*, 6, 754 2007.
 [14] J. S. Garitaonandia, M. Insausti, E. Goikolea, M. Suzuki, J. D. Cashion, N. Kawamura, H. Ohsawa, I. G. de Muro, K. Suzuki, F. Plazaola, and T. Rojo, *Nano Letters* 8, 661, 2008; J. de la Venta, A. Pucci, E. F. Pinel, M. A. García, C. J. Fernandez, P. Crespo, P. Mazzoldi, G. Ruggeri, and A. Hernando, *Adv. Mater.* 19, 875, 2007; P. Dutta, S. Pal, and M. S. Seehra, M. Anand, and C. B. Roberts, *Appl. Phys. Lett.*, 90, 213102, 2007.
 [15] G. Lopes, J. M. Vargas, S. K. Sharma, F. Beron, K. R. Pirota, M. Knobel, C. Rettori, and R. D. Zysler, *J. Phys. Chem. C*, 114, 10148, 2010.
 [16] K. M. Harbola and V. Sahni, *Phys. Rev. B* 37, 745, 1988; H. Hori, Y. Yamamoto, T. Iwamoto, T. Miura, T. Teranishi, and M. Miyake, *Phys. Rev. B* 69, 174411, 2004.
 [17] M. A. Muñoz-Márquez, E. Guerrero, A. Fernández, P. Crespo, A. Hernando, R. Lucena, and J. C. Conesa, *J. Nanopart. Res.* 12, 1307, 2010.
 [18] P. Crespo R. Litran, T. C. Rojas, M. Multigner, J. M. de la Fuente, J. C. Sanchez-Lopez, M. A. Garcia, A. Hernando, S. Penades, and A. Fernandez, *Phys. Rev. Lett.* 93, 087204, 2004.
 [19] I. Coulthard, I. S. Degen, Y. Zhu, and T. K. Sham, *Can. J. Chem.* 76, 1707, 1998.
 [20] D. Zhanchetet, H. Tolentino, M. C. Martin Alves, O. L. Alves, and D. Ugarte, *Chem. Phys. Lett.* 323, 167, 2000.
 [21] P. Zhang and T. K. Sham, *Appl. Phys. Lett.* 81, 736, 2002.
 [22] I. L. Garzón, C. Rovira, K. Michaelian, M. R. Beltrán, P. Ordejon, J. Junquera, D. Sánchez-Portal, E. Artacho, and J.M. Soler, *Phys. Rev. Lett.* 85, 5250, 2000.