P H Y S I C A L   R E V I E W   L E T T E R S

Fe Impurities Weaken the Ferromagnetic Behavior in Au Nanoparticles

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In this Letter, we report on a crucial experiment showing that magnetic impurities reduce the ferromagnetic order temperature in thiol-capped Au glyconanoparticles (GNPs). The spontaneous magnetization of AuFe GNPs exhibits a fast decrease with temperature that contrasts with the almost constant value of the magnetization observed in Au NPs. Moreover, hysteresis disappears below 300 K. Both features indicate that Fe impurities reduce the high local anisotropy field responsible for the ferromagnetic behavior in Au GNPs. As a consequence, the amazing ferromagnetism in Au NPs should not be associated with the presence of magnetic impurities.

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The experimental observation of a ferromagnetic (FM) behavior, characterized by magnetic hysteresis up to room temperature (RT) in thiol-capped gold nanoparticles (NPs) [1] and giant magnetization values and anisotropy in thiol-capped Au thin films [2], is attracting a broad interest. First, there is a great challenge in understanding the physical mechanism inducing FM-like behavior in systems that are far from being ferromagnetic. Second, the possibility of combining nanoscale with permanent magnetism up to human body temperature and a good biocompatibility, as occurs for gold, opens a wide range of future biomagnetic applications such as ferrofluids in molecular imaging, tumor targeting, and hyperthermia.

The electronic properties of NPs are different from that of their bulk counterparts due to the so-called size and surface effects [3]. Hence, modifications of the magnetic behavior could be expected by decreasing particle size to the nanoscale and/or surface modification. One strategy is the modification and tuning of the electronic properties of NPs by appropriate functionalization [4]. Those changes have been experimentally observed by x-ray photoemission spectroscopy in alkanethiol stabilized Au NPs [5] and through the FM behavior of thiol-capped Au and Pd NPs [1,6], both non FM in bulk state. The case of Au NPs is particularly interesting since bulk Au is diamagnetic. Moreover, this striking FM behavior is not observed when the Au NPs are stabilized with a surfactant. A similar tendency is observed in appropriate functionalized Au thin films [2].

From the above reported results, it turns out that the appearance of a magnetic moment should be associated to surface functionalization with strong interacting thiol derivatized species as well as with the reduction of particle size to the nanoscale. As inferred from extended x-ray absorption near-edge structure (XANES), capping promotes a charge transfer from Au atoms to organic chains [1,4,7]. Huge values of spin-orbit splitting, around 0.4 eV,

have been measured in Au surfaces [8]. The localized character of the magnetic moments, inferred from surface plasmon resonance studies (SPR) [9], as well as its orbital character, which implies a high magnetic anisotropy, have been proposed as the mechanism responsible for the ferromagnetic-like behavior [10].

However, the possible influence of magnetic impurities is always an important concern. In this Letter, we report on the magnetic behavior of thiol-capped Au glyconanoparticles (GNPs) where Fe impurities have been introduced in a controlled way [11]. The properties will be compared with that exhibited by high purity Au NPs. From these results, it can be concluded that the FM behavior should be inherently associated with the modification on the electronic structure of Au NPs and not to the presence of FM impurities.

Thiol-capped AuFe and Au GNPs stabilized by maltose and lactose neoglycoconjugates with different Au:Fe, and Au:S ratios have been studied. GNPs were prepared in aqueous solution by one step synthesis developed by Penadés *et al.* [11,12]. Table I summarizes the studied samples. Particle size distribution histograms were measured from transmission electron microscopy micrographs using an automatic image analyzer. Magnetic characterization has been carried out with a SQUID magnetometer. The magnetization of the NPs was obtained after subtracting the diamagnetic contribution of the sample holder. SPR has been measured by means of UV-VIS optical absorption.

TEM micrographs show monodispersed particles with an average particle size of around 1.8 and 2 nm, respectively, for samples stabilized with maltose and lactose neoglycoconjugates [7,11]. From these values, the number of atoms in the cluster and in the surface is estimated following [13]. The average composition, obtained by inductively coupled plasma (ICP) analysis, and the percentage of Au atoms bonded to a thiol group (by assuming that each available S is bonded to a surface Au atom), is also

TABLE I.   Summary of the structural characteristics of Au and AuFe GNPs. The estimated values of the anisotropy constant are also included.

Sample	Composition[a]	Av NP size (nm)[b]	Total Nr %Nr[c]	Av. composition of cluster (at.%)	Au:S	% surface Au atoms bonded	Volume Au bonded (nm^3) (4)[d]	$K (J/m^3)$
Au-SRmaltose	$(C_{23}H_{44}O_{11}S)_{201}Au_{201}$ 27 wt.% Au	1.8 nm	201 at/cluster 63.7%	Au_{100}	1:1	100%	2.5	4×10^7
AuFe1-SRmaltose	$(C_{23}H_{44}O_{11}S)_{191}Au_{191}Fe_{10}$ 23.7 wt.% Au 0.3 wt.% Fe	1.8 nm	201 at/cluster 63.7%	$Au_{95}Fe_5$	1:1	100%	2.5	2×10^7
AuFe2-SRmaltose	$(C_{23}H_{44}O_{11}S)_{533}Au_{198}Fe_3$ 12.1 wt.% Au 0.06 wt.% Fe	1.8 nm	201 at/cluster 63.7%	$Au_{98.5}Fe_{1.5}$	1:2.7	100%	2.5	0.7×10^7
Au-SRlactose	$(C_{20}H_{37}O_{14}S)_{98}Au_{314}$ 54 wt.% Au	2 nm	314 at/cluster 55.4%	Au_{100}	1:0.3	56.3%	1.9	6×10^7
AuFe-SRlactose	$(C_{20}H_{37}O_{14}S)_{95}Au_{266}Fe_{48}$ 51 wt.% Au 2.8 wt.% Fe	2 nm	314 at/cluster 55.4%	$Au_{84.7}Fe_{15.3}$	1:0.4	54.6%	1.9	2×10^7

[a]Composition determined from ICP analysis.
[b]Average particle size as calculated from particle size distribution histograms.
[c]Total Nr: calculated number of atoms for a pure gold cluster. %Nr: percentage of atoms located at the surface of a pure gold cluster.
[d]Estimated volume corresponding to surface Au atoms bonded to S.

indicated in Table I. $Au - L_3$ edge XANES spectra indicates a charge transfer from Au atoms to the thiol derivatized molecule [7].

Magnetic hysteresis up to RT is observed for both Au GNPs, see Fig. 1, confirming previous results [1]. The amount of Fe impurities (below 00.01 ppm) is not enough to account for the magnetization values. Thus, the magnetization should arise from the charge transfer that takes place upon bonding. The inset shows a non negligible coercivity present even at RT, decreasing from around 100 Oe at 5 K down to 30 Oe at 300 K. In the case of Au-SRLactose, a diamagnetic component is observed at RT (subtracted from the data plotted in Fig. 1), which is absent for Au-SRMaltose sample. According to the Au:S ratio, see Table I, not all surface Au atoms are bonded to a thiol group for the Au-SRLactose sample. Thus, a diamagnetic contribution arising from the core of the NP as well as from surface atoms not linked to thiol, and presumably from lactose, is resolved. When the magnetization is normalized to the amount of (estimated) Au bonded, see Table I, the magnetization values, at 5 K, become much more similar, $M_{Au-SRmaltose} = 0.134$ emu/g and $M_{Au-SRlactose} = 0.08$ emu/g. From these values, the magnetic moment of a bonded Au atom is estimated to be $\mu_{Au} = 0.0047\mu_B$ and $\mu_{Au} = 0.003\mu_B$, for Au-SRmaltose and Au-SRLactose, respectively. The quite similar values of the μ_{Au} provide further evidence that the appearance of a net magnetic moment should be undoubtedly attributed to the charge transfer that occurs through Au-S bond. It is worth it to remark that magnetic hysteresis is observed at RT, which implies that magnetic moments should be frozen due to an enormous local anisotropy field; i.e., the anisotropy constant should be, at least, of the order of 10^7 J/m³. This value is estimated by

comparing thermal energy, k_BT, and anisotropy energy, kV (k stands for the anisotropy constant and V for the volume occupied by surface Au atoms bonded to thiol). The estimated k values are summarized in Table I and should be taken as a lower limit since it has been considered a temperature of $T = 300$ K.

The thermal dependence of the magnetization also points out that Au GNPs behave in a very peculiar way
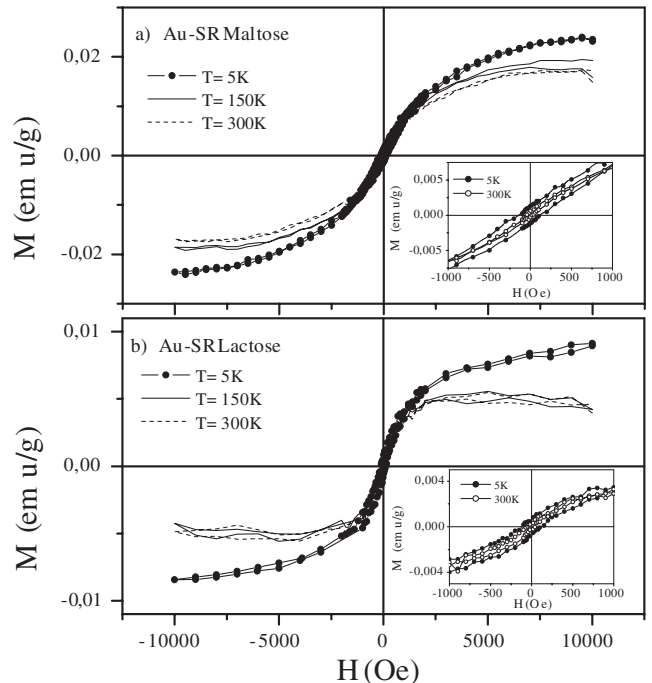

FIG. 1.   Magnetization curves of (a) Au-SRMaltose and (b) Au-SRLactose. The inset shows the hysteresis even at 300 K.

since they exhibit very little dependence with temperature
(Fig. 2), remaining almost constant up to 300 K. The lack
of thermal demagnetization process points out that ex-
change interactions between the magnetic moments, if
present, are not the main mechanism to be invoked to
account for the ferromagnetic-like behavior exhibited by
thiol capped Au GNPs, but rather an extremely high local
magnetic anisotropy that blocks the magnetic moments.

The magnetic behavior changes considerably upon Fe
impurities addition. Figure 2 compares the magnetization
thermal dependence for AuFe GNPs with that of Au GNPs.
The magnetization is normalized to the weight percentage
of Fe and estimated Au atoms bonded to thiol. It is clear
that Fe impurities modify the thermal dependence of mag-
netization, but not as expected. Although low temperature
magnetization increases with increasing Fe content, it is
inferred that Fe impurities are hardly responsible for the
anomalous thermal dependence found in Fe free samples.
For the three sets of AuFe GNPs, a sharp decrease of the
magnetization at very low temperatures is observed that
can be attributed to the Fe impurities behaving as para- or
superparamagnetic. For very small Fe additions (maltose
samples), the magnetization exhibits a further decrease
upon increasing temperature, reminding that of a Curie
temperature, around 180 K and 75 K for AuFe1-
SRmaltose and AuFe2-SRmaltose, respectively. In the
case of AuFe-SRLactose sample, where the amount of Fe
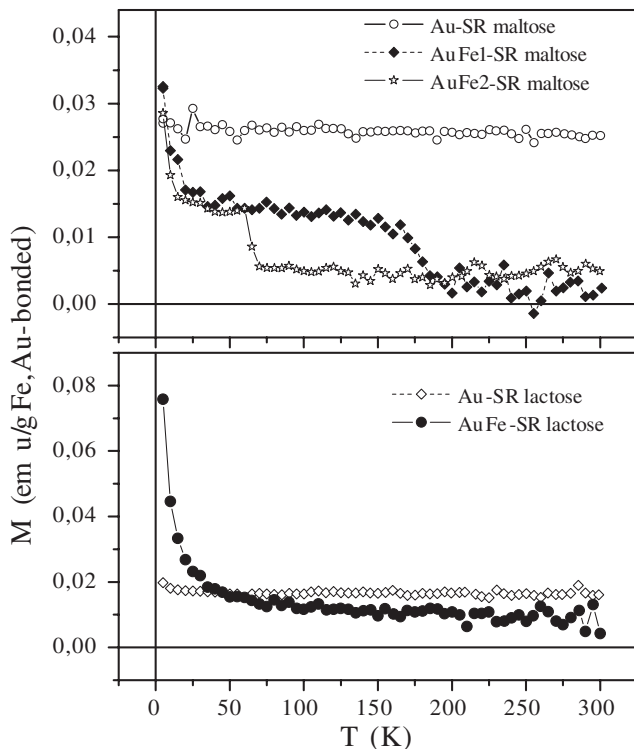is much higher, it is observed that the magnetization values

are smaller than for Au-SRLactose for temperatures above
75 K, showing a stronger temperature dependence.
Moreover, magnetization curves for the three sets of
AuFe NPs also point out that Fe impurities do not enhance
hysteresis, but contribute to its disappearance, whereas
they enhance the magnetization at 5 K. Figure 3 shows
the magnetization curves for AuFe2-SRmaltose and AuFe-
SRLactose samples. In all cases, hysteresis is observed at
5 K, although the values of coercive field are much smaller
than for Au GNPs. The sample with lower Fe content
exhibits the highest coercivity at low temperatures. An
estimation of the anisotropy constant is summarized in
Table I. In contrast with the behavior of Au GNPs, at
300 K a linear dependence of the magnetization with
applied field is observed for AuFe GNPs.

The main conclusion is that Fe impurities reduce the
strong local anisotropy field present at surfaces of Au NPs.
However, the mechanism responsible for the weakening of
the FM behavior by the presence of $3d$ impurities is not
clear. The differences between the AuFe-SRmaltose and
AuFe-SRlactose samples could arise from the different
Au:Fe ratio. AuFe is a binary system characterized by a
high enthalpy of mixing and little mutual solid solubility.
For instance, at 200 °C, Fe can be dissolved into Au up to a
2 at.%. According to the Au:Fe ratio, it can be expected
that in AuFe-SRmaltose samples, Fe is almost fully dis-
solved into the Au NPs forming some kind of Au(Fe) dilute
phase, whereas for AuFe-SRLactose small clusters of Fe
atoms that behave as superparamagnetic could coexist
together with the diluted Au(Fe) phase, contributing to
the magnetization but not to the hysteresis.

FIG. 2. Thermal dependence of the magnetization for Au and
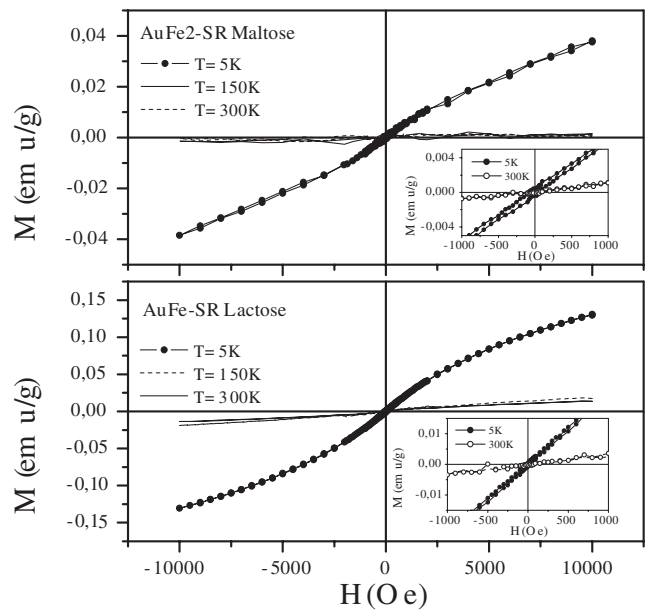AuFe GNPs measured under an applied field of 500 Oe.

FIG. 3. Magnetization curves of AuFe GNPs. Notice that in
contrast with the behavior exhibited by Au GNPs, hysteresis is
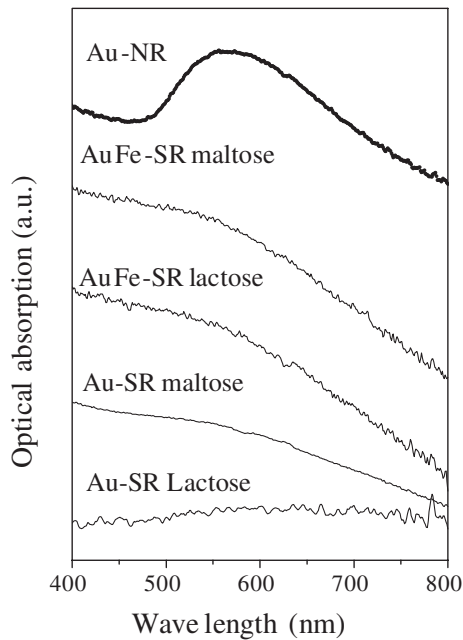not observed at 300 K.

FIG. 4. UV-Visible absorption spectra for the Au and AuFe GNPs. The spectrum of Au NPs stabilized by surfactant (that exhibit a diamagnetic behavior) is also included.

SPR measurements are shown in Fig. 4. The spectrum corresponding to $2-3$ nm bare Au NPs dispersed with a surfactant (Au-NR) which exhibits a diamagnetic behavior it is also shown. The later shows a broad absorption band centered at about 550 nm associated to the so-called surface plasmon resonance [14], due to the itinerant character of the $5d$ holes in diamagnetic Au NPs. This band becomes broader for the AuFe GNPs and is almost suppressed in the case of Au GNPs. These features are an indication of the increase of the damping of electrons due to charge localization at the surface [9] promoted by the strong interaction between surface Au atoms and thiol capping molecules. The presence of Fe promotes delocalization with respect to Au GNPs. Since the peculiar magnetism observed at nanoscale for Au GNPs has been shown [1] to be associated with localized moments, the effect of Fe is to reduce this permanent magnetism. However, the paramagnetic magnetization of Fe atoms contributes to the overall magnetization, mainly at low temperatures, but follows a Curielike law as observed in Fig. 2.

It has been shown that Fe impurities weaken the FM-like behavior exhibited by thiol-capped Au GNPs. Impurities reduce the spontaneous magnetization as well as the strong local anisotropy that blocks the bond-induced magnetic moments. The FM-like behavior in thiol-capped Au NPs has its origin on the charge transfer due to the strong interaction between surface Au-capping molecules, in combination with charge localization and the high value of the spin-orbit coupling in gold surfaces. The almost temperature independent value of the magnetization observed in the Au GNPs samples indicates that the thermal demagnetization process does not follow the typical law that applies in FM elements. In consequence, other mechanisms different from that of the exchange interactions should be invoked. In fact, coupling of orbital momenta have been recently proposed as to be the origin of FM-like behavior in thiol-capped Au NPs [10].

In summary, ferromagnetic behavior observed in thiol-capped Au NPs cannot be ascribed to the presence of magnetic impurities, that, opposite to what is expected, tend to destroy the ferromagnetic behavior.

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