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Ferromagnetism in bare gold nanoagglomerates produced by nanocluster deposition

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ABSTRACT

Recent research has shown unconventional magnetic properties in nanosized gold systems. These effects have mostly been detected in functionalized gold nanoparticles as well as in gold nanocrystalline films. We demonstrate ferro- and superparamagnetic behaviour in assemblies of bare gold nanoclusters. This is demonstrated by the characteristic ferromagnetic hysteresis with the temperature dependent saturation magnetization, remanence and coercivity in aggregates of small clusters. The detected magnetization is caused by the interaction between the separate clusters exhibiting an core-shell structure, and dependent on the total amount of gold confined in the samples. The behaviour is analogous to that of transition metal clusters.

1. Introduction

Bulk gold is well known to be diamagnetic. Recently however there have been both experimental and theoretical work indicating that departure from diamagnetism develops, while going down to nanoscale gold systems. These effects have mostly been exhibited by gold nanocrystalline films as well as functionalized gold nanoparticles [1]. Only a few papers have been published on the ferromagnetic behaviour of separate bare gold nanoclusters, these do not however treat the total volume dependence of magnetic behaviour in gold [2–5].

It is believed that the observed magnetic behaviour that departures from the bulk diamagnetism is an intrinsic property of nanosized gold with large surface-to-volume ratio [6–9]. Computer simulations also predict size-dependent spin polarization and ferromagnetism in bare gold nanoparticles and thin films due to the effect of surfaces at the nanoscale and strong spin–orbit coupling in gold [10–13]. Different available theoretical models that predict and explain the positive magnetization and ferromagnetism in bare gold nanoparticles as well as experimental results differ in detail. Overall they still have a common denominator, which is the existence of a core-shell magnetic structure with a bulk-like diamagnetic core and a shell of differently ordered surface magnetic moments [10–15].

Sato et al. have investigated the temperature dependence of Au nanocluster magnetization as well as the impact of exposure to air on their magnetization [3,2]. Li et al. have investigated the intrinsic magnetic moment of 4 nm bare face-centered cubic (fcc) Au nanoparticles [4,5]. Previously the size- and temperature dependent structural transitions in gold nanoparticles have been studied [16], but not in the connection with their magnetic properties. Further experimental studies into the behaviour of similar systems is desirable.

Previously we have reported on the ferromagnetism in nanocrystalline gold thin films [17]. In this work we contribute to the controversial subject of magnetism in gold nanostructures, by presenting experimental evidence of ferro- and superparamagnetic behaviour in assemblies of Au nanoclusters and complement the available data existing for thin films and individual gold clusters. It is shown that the magnetic behaviour depends on the total amount of gold confined in the samples.

Magnetic phenomena are very sensitive to the atomic environment. As the cluster interactions change due to changes in interaction range and degree, the magnetic behaviour is also influenced. When clusters are separate from each other (below the percolation threshold) long range dipolar forces and short range exchange forces act. As isolated particles evolve by agglomeration, exchange-coupled agglomerates will be produced. The agglomerates interact with each other via dipolar forces. When the percolation threshold is exceeded the behaviour of cluster assemblies is dominated by inter-cluster exchange coupling [18]. According to

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Löffler et.al. the exchange interaction at the boundaries between particles is weaker than the intra-particle atomic exchange which further reinforces the image of separate but interacting clusters [19]. Chudnovsky et al. [20–22] have studied the magnetic behaviour of nanostructured ferromagnetic materials. They have described how an increase in the inter-particle exchange of the cluster configurations evolves to a correlated super-spin glass (CSSG) in which the magnetization vectors of neighbouring particles are nearly aligned. The disordered CSSG state is fragile and application of a small field will produce a 'ferromagnet with wandering axes' (FWA). If gold clusters are ferromagnetic they should also produce similar effects as they start to interact at close proximity and overcome the percolation threshold. Therefore, our goal in this work was to observe experimentally how magnetization of gold nanoagglomerates depends on their aggregation state that allows to conclude on ferromagnetism in bare gold nanoclusters.

2. Materials and methods

In the present work bare gold nanoparticles were produced with a condensation-cell-type cluster aggregation source (NC200, Oxford Applied Research), charged with a gold target of 99.999% purity. The gold clusters were deposited at room temperature directly on a template, a lightweight homogeneous plastic straw provided by Quantum Design as a sample holder for ultrahigh-sensitivity measurements. The magnetic properties were evaluated using an ultra-high-sensitive magnetometry based on a superconducting quantum interference device, SQUID (Quantum Design MPMS-XL7), providing a magnetic field up to 70 kOe at temperatures from 1.8 to 400 K.

Before the actual SQUID measurements of the nanocluster deposited gold, the background signal caused by the templates shape, local deformations, material defects, and non-homogeneity was measured. This was done by measuring the template (with no gold deposited) with all of the experimental conditions the same as during the actual measurements. The resulting data was then subtracted from the actual magnetization data measured from gold deposited in the templates. This was done in order to verify that the presented results originate only from the deposited gold.

Special care was taken to prevent the deposited gold as well as the template to be exposed to parasitic magnetic impurities. To ensure that the effect from native impurities in the substrate and deposited gold was negligible, the impurity level was evaluated by inductively coupled plasma (ICP) mass spectrometry and elastic recoil detection analysis (ERDA), after the magnetization measurements. With all the precautions taken the total concentration of all trace elements in the gold as well as the template were at a level of 10 ppm, and thereby these impurities do not influence our results [17].

The morphology of the samples was examined by high-resolution transmission electron microscopy, HR-TEM (JEOL JEM-2200FS) and atomic force microscopy, AFM (Veeco AutoProbe CP-Research). For the HR-TEM measurements the gold clusters were deposited on carbon holey films 12 nm thick (Quantifoil Micro Tools GmbH). We assume that the morphology of the deposited gold was not affected by the templates, as both the Quantifoil carbon film and the material for the plastic straws used in the magnetization measurements are chemically non-reactive. In the Supplementary Information a X-ray diffraction (XRD) pattern for a deposited sample is shown.

3. Results and discussion

The energy of deposited Au clusters in our case was 0.3 eV per atom [17,23,24]. This leads to the formation of well developed branches and porous like morphology of the resulting sample. The clusters act as building blocks, softly landing on top of each other and undergoing minor agglomeration [25]. The developed morphology of our samples, is a result of unavoidable coalescence and coarsening of the clusters on the template at the deposition temperature. For example a 20 min deposition results in a fragmentary morphology of partly interconnected gold aggregates, whereas a 1 min deposition produces a dispersion of separate gold particles, see Fig. 1. Based on rigorous image analysis of HR-TEM micrographs, similar to those presented in Fig. 1, about 7.9 ± 1.1% of the surface area of the 1 min deposited sample was covered with Au clusters, with an average cross-sectional area of 26 nm^2. Derived from AFM measurements the corresponding cluster height is 5.1 ± 1.8 nm. As the cluster shape is noted to be a slightly flattened sphere, the total volume of the gold confined in the sample deposited for 1 min is estimated to be $(2.5 \pm 0.6)10^{-8}$ cm^3. By varying the deposition time the volume of the gold confined in the analysed samples could be adjusted, as the deposited volume is linearly dependent on deposition time. In this work three different samples, with different volumes of gold, were analysed, see Table 1.

In Fig. 1 it can be seen that after 1 min deposition the clusters are well separated. The situation will change after 5 min and the probability for a significant interaction between two clusters is then higher but frequent coalescence of clusters is not yet probable. As cluster dose is increased cluster coalescence will also increase. This leads to a lower surface-to-volume ratio for the samples with a higher cluster volume, with the lowest value occurring for sample C. According to AFM images there is only a 10-fold increase in surface area for sample C, the corresponding volume increase is 20-fold for the 1 min sample. The interaction between clusters depends on remaining boundaries and thereby also affects the interacting spins.

Magnetization measurements were performed on all samples (Table 1), but no magnetic signal could be detected after 1 min deposition. Fig. 2 shows magnetization of the deposited nanoparticle samples. The magnetization is seen to exhibit characteristic ferromagnetic hysteresis of the samples B and C with the remanent (M_R) and saturation (M_S) magnetizations only slightly changing

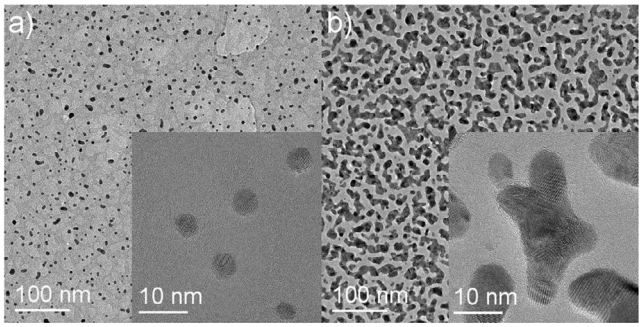

Fig. 1. HR-TEM micrographs of (a) single clusters by 1 min deposition and (b) cluster-assembled aggregates by 20 min deposition (sample C).

Table 1
Summary of the samples showing the total volume of Au confined in them and the deposition time.

Sample	Symbol	Deposition time (min)	Volume 10^{-8} (cm^3)
		1	2.5 ± 0.6
A	▲	5	12.5 ± 2.9
B	■	10	25.0 ± 5.7
C	•	20	49.9 ± 11.4