Magnetic disorder in nanostructured $F_{7}Au_{93}$ films and $F_{14}Au_{86}$ powders

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Abstract. Thin films and powders of dilute Fe-Au alloys have been produced by DC-magnetron sputtering and high-energy milling, respectively. Energy dispersive X-ray spectroscopy gives $F_{7}Au_{93}$ for the films and $F_{14}Au_{86}$ for the powders. The film, with a thickness below 200 nm measured by atomic force microscopy, was deposited onto a Si(100) substrate. X-ray diffraction reveals a major presence of $fcc-Au$ peaks masking the $bcc-Fe$ phase. The (10-300 K) DC-susceptibility ($H = 100-1000$ Oe) shows a clear cusp in the films in contrast to the powders, with a reentrant spin glass-like behavior.

1. Introduction
The study of systems comprising magnetic nanoparticles embedded in different matrices has gathered a vast attention since many years ago. The appeal of these systems arises from the complexity and variety of the magnetic interactions among the magnetic nanoparticles, as well as the technological potential based on, for instance, giant magnetoresistance or ultrasoft magnetic properties [1]. If the magnetic nanoparticles are relaxing individually behave as a superparamagnet but when the concentration of particles is increased, exchange, RKKY or dipolar interactions, may come into play. In this scenario, the magnetic relaxation of the particles is modified resulting in behaviours like interacting superparamagnetism [2], cluster superspin glass [3] or superferromagnetism [4]. A procedure to better understand the relaxation is using matrices of different nature. In this sense, it is of particular interest the use of diamagnetic matrices such as Au, Cu or Ag. Outstanding reports for the scrutiny of magnetic disorder were published in bulk alloys of Fe-Au decades ago [5, 6]. The granular (and layered) nature of several recent nanostructures supports a renovated interest of producing similar Fe-Au alloys with different fabrication procedures which may lead to curious arrangements of the magnetic nanoparticles inside the matrix.

We are aiming here to compare the effect of the nanoscopic structure in the magnetic response of Fe particles embedded in Au. This has been pursued by preparing Fe-Au powders (mechanical alloying) and thin films (DC-magnetron sputtering) below the percolation limit ($\sim 28$ at.%) [7]. It is particularly challenging to deal with the thin monolayered films for which the magnetic response is extremely weak to detect.

2. Experimental
Diluted $F_{x}Au_{100-x}$ ($x$, atomic concentration) alloys were prepared in both thin film and powder forms taking into account the high immiscibility between Fe and Au. The thin films were
prepared by the magnetron DC-sputtering method with an Ar$^+$ plasma of 0.1 KW hitting the target. The powders were obtained by milling elemental Au and Fe (99% purity) inside WC containers under an Ar atmosphere. The milling was performed during 70 hours, with 1 hour pauses to avoid an excessive heating. The thin film thickness was measured by atomic force microscopy (AFM) and the chemical composition of both samples was checked by energy dispersive X-ray spectroscopy (EDX) in several areas of each sample. X-ray diffraction (XRD) patterns (Cu-K$_\alpha$) were collected during 4 days. Zero Field Cooled/Field Cooled (10 K - 300 K) sequences have been performed in a QD MPMS for the thin films and in a QD PPMS for the powders, in magnetic fields $H$, 100 $\leq$ $H$ $\leq$ 1000 Oe.

### 3. Results and discussion

EDX measurements provide the chemical composition of the $Fe_xAu_{100-x}$ samples. A value of $x = 14\pm1$ was obtained for the powder, and $x = 7\pm1$ for the thin film, both showing a great compositional homogeneity. The XRD diffractogram (Figure 1) of the thin film shows a predominant crystalline structure stemming from the majority (93 at.%) fcc-Au phase with a lattice parameter of $a = 4.05(2)$ Å (pure Au, $a = 4.078(1)$ Å). A (111) preferential orientation of the Au grains in the film can be inferred from the relative peak intensities of the pattern. In this pattern it is equally evident the large (inevitable) contribution from the Si substrate. Other sputtered films around $Fe_{20}Au_{80}$ report the presence of crystalline Fe nanograins [8]. The powder $Fe-Au$ XRD pattern (not shown) also displays the predominant fcc-Au peaks and is very similar to those recently reported of nanometric $Fe-Cu-Ag$, in which bcc-$Fe(Cu)$ 4.5 nm grains are embedded in a fcc-Ag matrix [3]. Given the certain presence of Fe (from EDX), it is clear that the bcc-$Fe$ is masked due to the total overlapping of the Fe peaks with some of the Au reflections, a problem also reported in the mentioned $Fe-Cu-Ag$ alloys. Finally the large form factor of the Au ($Z = 79$) respect to Fe ($Z = 26$) also contributes to the actual masking. In the inset of Figure 3, a profile of the film shows that the monolayer thickness reaches 200 nm.

![Figure 1](image-url)

**Figure 1.** XRD pattern of the thin film sample in logarithmic scale to enhance the diffraction of the monolayer respect to the preferred Si(100) substrate and Au(111) reflections. The inset shows the 200 nm thickness of the film obtained by AFM.

The most salient result of the ZFC/FC DC-susceptibility curves is the presence of a magnetic irreversibility in both powder and film alloys, as can be seen in Figures 2 and 3. This irreversibility (larger for the powdered alloys) is usually taken as a sign for the presence of
magnetic disorder and/or cluster presence [1, 4]. However, and despite their similar chemical composition, a couple of remarkable differences in the magnetic response are observed in both the ZFC and FC curves.

![Figure 2](image-url)  
**Figure 2.** Irreversibility in the ZFC/FC and cusp at \( T = 30 \) K in the ZFC static susceptibility at 100 and 1000 Oe of the \( \text{Fe}_7\text{Au}_{93} \) thin film.

On the one hand, the thin film shows an asymmetric cusp (in ZFC and FC) and a paramagnetic-like fall above the peak temperature for both applied fields. It is also noticeable the extremely small signal for the \( \text{Fe}-\text{Au} \) film, concomitant to the low \( \text{Fe} \)-content (7 at. %) and thickness (200 nm). This susceptibility was corrected from the diamagnetic negative signal from the Si(100) substrate. On the other hand, the \( \text{Fe}-\text{Au} \) powder does show a decrease of magnetisation for temperatures below 100 K, as it is observed in the inset of Figure 3, where the susceptibility derivatives are plotted. The field in the powders affects the onset of their low temperature kink in ZFC \( H = 100 \) Oe and \( H = 500 \) Oe.

![Figure 3](image-url)  
**Figure 3.** Irreversibility in the ZFC/FC susceptibility at 100 Oe of the \( \text{Fe}_{14}\text{Au}_{86} \) powder. Inset: Derivatives of the ZFC branch with a marked upturn. Lines are guides for the eyes.

*Bulk* \( \text{Fe}_8\text{Au}_{92} \) produced in the form of mm diameter spheres was reported to display a sharp asymmetric peak [5] (smeared when a biasing \( DC \) field of \( H = 100 \) Oe is applied) as recorded in AC susceptibility with an excitation field of 5 Oe and low frequency of 155 Hz. In such a case the peak is centred around 27 K, in agreement with our case. The peak is less clear in the
FC susceptibility. The comparison between the $H = 100$ Oe and $H = 1000$ Oe curves evidences that the peak position is not greatly modified ($\lesssim 1$ K) but the shape is rounded for the larger field. Examining the data in ref. [5], it is possible to estimate (not performed there) the peak width for the bulk alloy reaching around 6 K. The presence of such a peak was ascribed to the freezing of magnetic clusters from a paramagnetic state in agreement with the well-studied spin glass behaviour. Nevertheless, in our case the peak width increases to 25 K. In consequence, the similar peak positions between bulk and film alloys reflects that the film nanostructure should consist of clusters of a similar average size but the increased peak-width in the film is a sign of a wider particle size distribution. The fall of the magnetic signal above the cusp in the film follows a Curie-Weiss law with a $\theta_p = -5$ K and a Curie constant value which allows to establish the presence of particles with a maximum estimated diameter around 3 nm (extracted from $H=100$ Oe signal). This size should be checked with other techniques (for example transmission electron microscopy) but in any case the particles relaxing superparamagnetically above the peak temperature. Additionally, a striking detail appearing in the films is the very low temperature increase for the FC curve. Some groups using $[\text{Co}_{80}\text{Fe}_{20}\text{Al}_2\text{O}_3]_{10}$ multilayers conclude that this upturn is a feature coming from tiny magnetic particles (in the sub-nanometer range) (glue particles) that may mediate the coupling of the bigger particles [9]. The small difference in the composition cannot be uniquely responsible for the change in the magnetic response of the powders and films studied here, but this diluted alloys are likely to be more affected by the structure at the nanoscopic scale. In the powder it seems that the coupling among particles is much stronger, giving rise to a ferromagnetic-like behavior at RT and a reentrant spin glass state (random anisotropy) settled in below 100 K. The coupling among particles must be weaker in the films to give rise to the observed behavior.

4. Conclusions

Fe-Au alloys with low Fe-content can be produced by mechanical milling and sputtering in the form of powders and films. The XRD patterns show a predominant fcc-Au phase masking most of the Fe-bcc contribution. The DC susceptibility curves (ZFC/FC process) show irreversibility for both alloys with similar compositions but in the films there is pronounced peak (barely affected by the applied field) whereas in the powder a reentrant spin glass-like behaviour is evident. Both behaviours are connected to the presence of nanoparticles which are magnetically more coupled in the powder. There is still an open question about the precise role of the average size and interparticle distance which we are already investigating by Transmission Electron Microscopy.

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