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Effects of thermal annealing on the magnetic interactions in nanogranular Fe–Ag thin films

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ABSTRACT

In this paper we have studied, by analysing the evolution of the magnetic behaviour during thermal treatment, the role of the interparticle magnetic interactions in Fe_xAg_{100-x} granular thin films prepared by sputtering deposition technique. Two compositions have been selected: $x = 25$ and 35, below and around the magnetic percolation of the system, respectively, according to our previous works. The structure of these thin films has been studied by X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) measurements. To analyse the magnetic behaviour, DC magnetic measurements have been carried out after progressively annealing the samples at different temperatures ($0 \leq T_{ann} \leq 200\,^{\circ}C$). These measurements have revealed that, upon thermal treatment, the frustrated state at low temperatures ($T < 80$ K) for the $x = 25$ sample tends to disappear, probably due to the weakening of RKKY interactions after the segregation of soluted Fe atoms in the Ag matrix. However, dipolar interactions are not affected by the annealing. On the contrary, at $x = 35$, around the magnetic percolation, the annealing gives rise to an increasingly ordered interface, thereby enhancing the transfer of the direct exchange interactions.

1. Introduction

The magnetic properties of the materials change drastically as we approach the nanometric scale [1,2]. Particularly interesting is the case of nanogranular materials composed of magnetic nanoparticles embedded in a solid matrix. By modifying the characteristics of the nanoparticles and the matrix, the physical properties of these materials can be tuned accordingly to the scientific or technological aim. In particular, the study of the magnetic interactions in this kind of systems has been of great interest because they not only give rise to a rich variety of magnetic behaviours [3–6] but also play a fundamental role in practical applications such as magnetic sensors, ultra-high density memory devices, or magnetoresistive recording heads [7–10].

Concerning the magnetic interactions, it has been observed that as the concentration of the magnetic material in the granular alloys increases, the magnetic interactions become more relevant and give rise to different phenomena [11,12]. At low concentrations, magnetic nanoparticles are well separated and therefore, predominant interactions are of long-range nature. It is well known that in granular systems with metallic matrices, two types of important interactions should be considered at the beginning: dipolar and Ruderman–Kittel–Kasuya–Yoshida (RKKY) [13]. As the content of magnetic material rises, the number and/or size of the nanoparticles increases, they become closer together, and stronger short range interactions appear, greatly dependent on the nature of the interface of the nanoparticles, such as direct-exchange, superexchange, or tunneling exchange interactions [12,14], which give rise to an increasing long-range order.

Fe_xAg_{100-x} granular thin films are ideal to study these phenomena since Fe and Ag present a high value of positive alloy formation energy (28 kJ/mol) [15], thereby being highly inmiscible and allowing us to obtain samples consisting of Fe nanoparticles embedded in a diamagnetic metallic Ag matrix. Their magnetic and magnetotransport properties have been studied in the literature [5,16–20].

In a previous work [20], we have carried out an in-depth analysis of the collective magnetic behaviours in these Fe_xAg_{100-x} samples, for an intermediate range of concentrations, $25 \leq x \leq 55$. In the sputtered samples, we have managed to keep the size of the nanoparticles practically constant while their number increased with increasing Fe content. A clear crossover in the collective magnetic behaviour was observed as a function of the Fe content, from a superspin glass (SSG) at low x to a superferromagnet (SFM) above the magnetic percolation ($x \sim 35$).

At low concentrations, $x < 35$, and high enough temperatures, the system behaves basically like an interacting superparamagnet (ISPM) [21]. As the temperature decreases, the system enters into a

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magnetically disordered or superspin glass state [22], mediated mainly by long-range interactions (dipolar and/or RKKY), the anisotropy of the nanoparticles and the spatial disorder. With increasing Fe concentration, the number of Fe nanoparticles increases, they become closer together, and a process of magnetic percolation takes place due to the more relevant role of direct exchange interactions. This enhances the long-range ferromagnetic order in the samples. At $x > 35$ the magnetic behaviour is more similar to the one expected for a superferromagnet [3].

Despite these thorough studies, there are still many questions concerning the nature and relevance of the different interparticle interactions that appear at these concentrations. In order to shed more light on this topic, first we have analysed the structure of these samples by X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) at the Fe K-edge. After that, we have performed an analysis of the evolution of the magnetic behaviour after thermal annealing. In addition to the typical segregation of diluted atoms [23–25], the annealing treatment also improves the samples microstructure by smoothing the clusters interface [26–28], making it more structurally ordered and relieving the lattice strain [39]. We will see how this affects the magnetic interactions in these Fe–Ag granular thin films.

2. Experimental details

In this paper, we have prepared by sputtering deposition technique two representative Fe_xAg_{100-x} granular thin films, one in the SSG regime, with $x = 25$, and the other one around the magnetic percolation, with $x = 35$. Details of the preparation can be found in ref. [20]. Their compositions were determined by energy dispersive X-ray analysis (EDX) and magnetometry. Concerning the structure analysis, X-ray diffraction measurements were performed using a Philips PW-1710 diffractometer, working at the Cu Kα wavelength. To avoid the very intense Si(4 0 0) Bragg peak, two separate diffractograms have been measured at the angular range before and after this peak. XAS measurements were carried out at the BM29 beamline of the European Synchrotron Radiation Facility (ESRF – Grenoble). All the spectra were obtained in a fluorescence setup and the measurements were carried out at room temperature, around the Fe–K edge energy (7112 eV), using a Si(1 1 1) monochromator, and reaching a maximum energy of $k = 13 Å^{-1}$ (~7756 eV).

Concerning the magnetic measurements, both zero-field cooling (ZFC) and field cooling (FC) data were collected. Magnetisation measurements were taken in the temperature range 5–300 K. For the thermal treatment, the samples were annealed during 1 h in an oven with N_2 atmosphere at different consecutive temperatures for the same piece of sample. The isothermal evolution of the magnetisation as a function of the applied field, up to 40 kOe, was also measured.

3. Results and discussion

3.1. Structural analysis

In order to properly study the role of the interactions in the magnetic properties of Fe_xAg_{100-x} granular thin films, we have carried out a preliminary analysis of their micro and nanostructure. In Fig. 1(a) we present the XRD pattern of the as-deposited $Fe_{25}Ag_{75}$ sample. As stated before, the Si(4 0 0) [Cu Kα] peak has been skipped. Apart from the peaks related to the Si substrate, only the fcc Ag(1 1 1) and (2 0 0) can be clearly distinguished. However some shoulders around the position of fcc Ag(2 2 2) and Ag(3 1 1) are also present. No diffraction peaks for the Fe have been observed: unfortunately, the main diffraction of Fe, bcc Fe(1 1 0), overlaps with that of Ag(2 0 0), and so, even if present, cannot be distinguished. Therefore, these results basically indicate that the Ag matrix is composed of highly textured crystalline grains, and that the Fe nanograins must be very small, at least, small enough so as not give diffraction peak.

We have tried to obtain some additional information about the amount of soluted Fe in the Ag matrix by carrying out a quantitative analysis of the fcc Ag(1 1 1) peak. Although the solubility of Fe and Ag is very low, as stated before, some concentration of soluted Fe atoms could be expected. The presence of soluted atoms in the matrix plays an important role in the interactions, specially

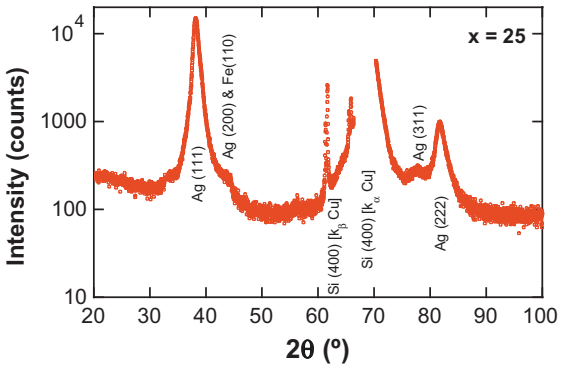

Fig. 1. XRD pattern (log. scale) of a $Fe_{25}Ag_{75}$ thin film. Labels indicate the positions of the different Bragg peaks.

concerning RKKY interactions [23–25]. Fig. 2 shows the fcc Ag(1 1 1) peak, together with the fittings to a typical pseudo-Voigt function [29], which is the averaged sum of a Lorentzian, $L(2\theta - 2\theta_0)$, and a Gaussian, $G(2\theta - 2\theta_0)$, functions:

$$I(2\theta) = I_{hkl}[\eta L(2\theta - 2\theta_0) + (1 - \eta)G(2\theta - 2\theta_0)] \quad (1)$$

being $2\theta_0$ the angular position of the corresponding peak, and η a parameter ($0 \leq \eta \leq 1$) related to the relative proportion of both contributions. We have checked, as can be seen in Fig. 2, that in order to obtain a good fitting it is necessary to include two fitting peaks. First one of them (peak 1) is centered around the expected position of fcc Ag(1 1 1) diffraction, while the second one (peak 2) is slightly displaced towards higher angles. We have checked that as the Fe content increases, this second peak progressively displaces towards higher angles, approaching the expected position for the bcc Fe(1 1 0) diffraction. This suggests that the first peak is related to a pure Ag crystalline phase with a lattice parameter close to the one corresponding to fcc Ag, $a_{peak1} = 4.09(1)$ Å, while the second one is associated to a phase of Ag with some soluted Fe atoms, being the obtained lattice parameter, $a_{peak2} = 4.03(1)$ Å. The concentrations of solute Fe atoms can be easily calculated from the shift in the Bragg diffraction of this second peak, if we assume the alloying of Fe and Ag follows the Vegard's law [30]. The calculated values indicate that around a 1% of the total Fe in the $Fe_{25}Ag_{75}$ thin film is soluted inside the Ag matrix. Similar results have been found for the $Fe_{35}Ag_{65}$ sample. Additionally, from these fittings we have obtained that the average size of the Ag crystalline grains is 11(1) nm.

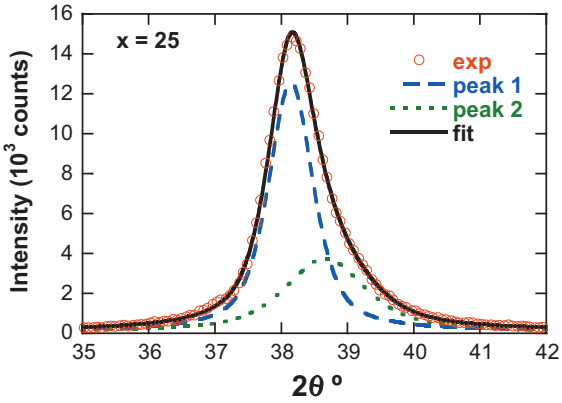

Fig. 2. Detail of the XRD pattern of a $Fe_{25}Ag_{75}$ thin film around the position of the fcc Ag(1 1 1) peak. Peaks 1 and 2 are the fitting peaks obtained from pseudo-Voigt functions.