Magnetic properties of electrodeposited Fe-poor Fe-Cu alloys

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In Fe-Cu alloys prepared by pulsed electrodeposition, Fe clusters form directly within a non-magnetic Cu matrix. The clusters contain around 140 Fe atoms and are superparamagnetic at room temperature. Below 160 K, it is proposed that the clusters order into a so-called superferromagnetic arrangement. This behaviour is ascribed to the persistence of weak exchange interactions mediated by isolated Fe atoms dispersed within the non-magnetic Cu matrix.

Keywords: Fe-Cu alloys, Fe clusters, Superferromagnetism, Electrodeposited alloys

I. INTRODUCTION

Magnetic nanoparticles may be characterized by a number of original properties which distinguish them from usual magnetic systems. As isolated objects, they may show enhanced magnetic anisotropy, non-collinear magnetic order or superparamagnetic behaviour [1]. As an ensemble of objects, they may reveal giant magnetoresistance [2] or Giant Hall effect [3]. As an ensemble of magnetically interacting objects, they may show diverse types of magnetic orders [4]. The present study is concerned with this last aspect more specifically. In usual magnetic systems, exchange interactions largely dominate over dipolar interactions. In contrast, in nanoparticle assemblies, exchange and dipolar interactions are often found to be of the same order of magnitude. This is due to the combination of two phenomena: (i) - the physical separation existing between the nanoparticles which implies that exchange coupling is much weaker than in usual systems and (ii) - the very large response to a weak magnetic field which is inherently associated to the large size of the nanoparticles magnetic moments.

With this in mind, we have undertaken a study of Fe-Cu alloys prepared by electrodeposition. Fe and Cu being immiscible, the objective was to find procedures leading to the formation of small Fe clusters within a Cu matrix, and obtain model systems for the study of magnetic interactions in nanoparticle assemblies. In the present paper, we focus on the Fe-poor part of the Fe-Cu phase diagram The properties of two samples are analysed more specifically, with composition $Fe_{10}Cu_{90}$ and $Fe_{30}Cu_{70}$ respectively.

II. FE-CU ALLOYS

Although Fe and Cu are immiscible elements, it is well known that Fe_xCu_{100-x} metastable alloys may be prepared by specific methods such as sputtering [5] or mechanical alloying [6]. Fe-rich alloys crystallize in the α-Fe bcc phase whereas Fe-poor alloys crystallize in the fcc phase of Cu. The x-value, typically between 60 and 80, at which the transition from bcc to fcc structure takes place depends on the preparation method used. Further, a certain range of x-values may exist for which both phases coexist.

Most generally, bcc alloys are ferromagnetic below their Curie temperature, which is much higher than room temperature. In a recent study, we have analysed the magnetic properties of electrodeposited Fe-Cu alloys [7]. In agreement with previous studies [8-9] we found that Fe-rich alloys are ferromagnetic with a Curie temperature significantly higher than room temperature and which decreases as the Fe content in the alloy is increased.

III. SAMPLE PREPARATION, CHEMICAL AND STRUCTURAL CHARACTERIZATION

The alloys concerned by the present study were in the form of films prepared by pulsed electrodeposition from a bath composed by: 0.01 or 0.001 M $FeSO_4.7H_2O$, 0.001 M $CuSO_4.5H_2O$, 1 M KC1, 0.1 M Na_2SO_4 and 2.2 10^{-2} M sodium citrate. A three-electrode conventional cell was used to deposit the alloys. The potentials were measured against a saturated calomel electrode (SCE), which was placed very close to the substrate surface to minimize the ohmic potential drop in the electrolyte. A platinum disc with a surface area of 1.7 cm^2 was used as anode. The substrates used in all electrochemical experiments were Si/Ti (20 nm)/Au (40 nm) with Ti and Au sputtered onto Si. The surface area exposed to deposit was 0.3 cm^2. Short current pulses (1 ms) were used to favor small grain size formation as well as to minimize hydrogen evolution during the electrochemical process. The film total thickness was about 100 nm. The alloy composition was determined by energy dispersive X-ray spectrometry (EDS) and by PIXE. For the two alloys described in the present study, the alloy composition was respectively $Fe_{10}Cu_{90}$ and $Fe_{30}Cu_{70}$. The films were structurally characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). They are formed of small crystallites, typically 40 nm in diameter. At the above mentioned compositions, the samples crystallize in the fcc phase, in agreement with previous studies [5,6,8].

IV. MAGNETIC MEASUREMENTS

Magnetization measurements were performed from low temperature (4.2 K) up to room temperatures using a SQUID magnetometer (Quantum Design, San Diego CA, USA). In the two considered samples ($Fe_{10}Cu_{90}$ and $Fe_{30}Cu_{70}$), the field dependence of the magnetization at different constant temperatures is characteric of ferromagnetic-like behaviour or superparamagnetic-like (i. e. involving clusters with Curie temperature above room temperature) behaviour (see sample $Fe_{10}Cu_{90}$ Figure 1). Due to the heterogeneous nature of magnetism in these systems, the nature of the low temperature magnetic order requires further analysis. With this in mind the temperature dependences of the low field FC and ZFC magnetizations (under $\mu_0 H_{app} = 0.02$ T) (Figure 2) were measured. In $Fe_{10}Cu_{90}$, the ZFC magnetization increases with temperature at low temperature. It shows a peak at about 120 K, and at higher temperature decreases with increasing temperature. The FC magnetization decreases monotonously with increasing temperature in the entire studied temperature range and the FC and ZFC magnetizations are superimposed above 135 K. These results confirm that magnetic clusters are present, which are superparamagnetic from room temperature to some intermediate temperature, below which the clusters become frozen.

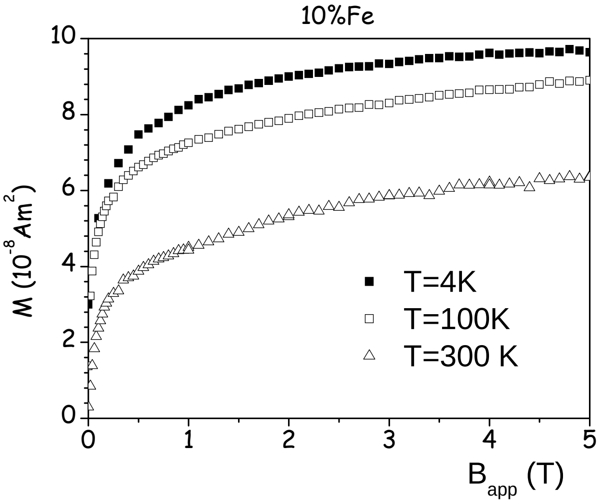

FIG. 1: Magnetization curves in $Fe_{10}Cu_{90}$ alloy at different temperatures

The temperature dependence of the inverse susceptibility in $Fe_{10}Cu_{90}$ derived from the FC magnetization curve of Figure 2 is shown in Figure 3. The high temperature part of the curve is a straight line which intercepts the temperature axis at 160K. This indicates that positive interactions exist between the clusters. The observed behaviour may be analysed within the molecular field model. From the sample volume value, $0.5\ 10^{-12} m^3$, the value of the cluster Curie constant, $C_{cluster}$, equal to the inverse of the slope of this line, is obtained as 12.3. $C_{cluster}$, may be expressed as :

$$C_{cluster} = \frac{N_{Fe}\mu_0 n_{Fe}\mu_{Fe}^2\mu_B^2}{3k_B} \tag{1}$$

where N_{Fe} is the number of Fe atoms per unit volume (85 10^{26} Fe atoms/m^3), n_{Fe} the number of Fe atoms in a cluster (the Cu atoms are assumed to be non-magnetic) and μ_{Fe} the Fe atomic moment assumed to amount to $2\mu_B$ (μ_B is the Bohr magneton). The n_{Fe} value derived from the experimental value of $C_{cluster}$ is 140.

The positive value of the paramagnetic Curie temperature, $\theta_c = 160K$, indicates that the clusters are coupled by dominant ferromagnetic interactions. The derived molecular field coefficient, $n (= \theta_C / C_{cluster}) = 13$ corresponds to a molecular field of 2.6 T. It may seem surprising that a paramagnetic Curie temperature of 160 K may be found for such a small molecular field value. However, one should consider that the large cluster magnetic moment may become magnetized under much smaller magnetic field than an atomic magnetic moment.

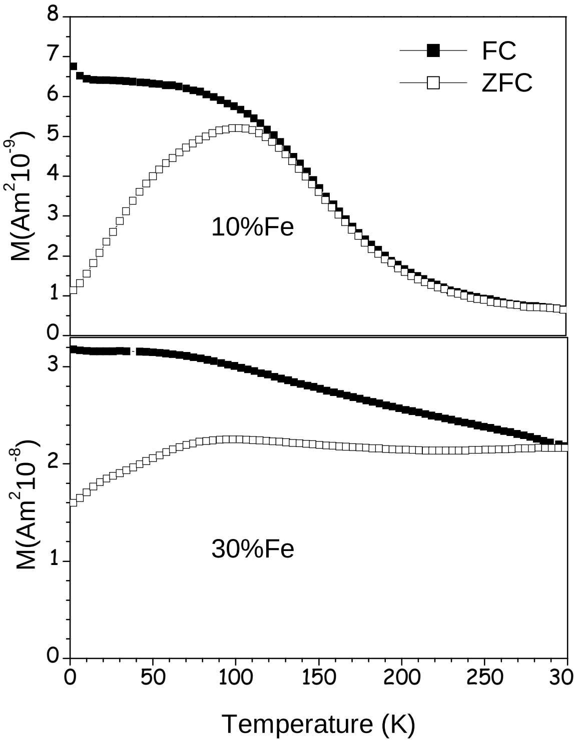

FIG. 2: Field Cooled (FC) and Zero Field Cooled (ZFC) magnetizations measured under an applied field of 0.02T, in the $Fe_{10}Cu_{90}$ and the $Fe_{30}Cu_{70}$ alloys.

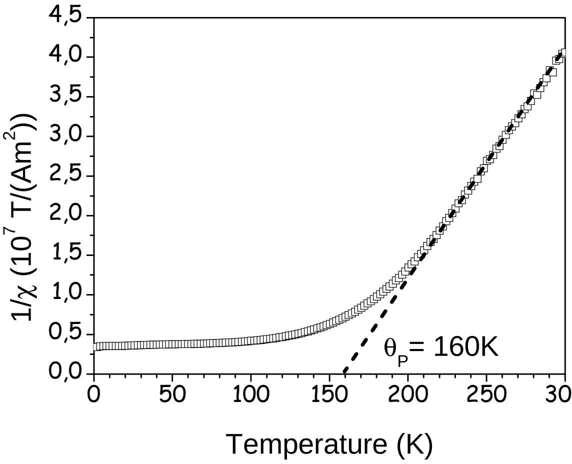

FIG. 3: Thermal variation of $1/\chi$ for $Fe_{10}Cu_{90}$. θ_P is the paramagnetic Curie temperature derived by extrapolation of the high temperature variation of $1/\chi$.

In sample $Fe_{30}Cu_{70}$, the temperature dependence of the FC/ZFC magnetizations suggests that a cluster-like contribution is superimposed to the normal ferromagnetic one. Although the clusters contribution shows similar behaviour as in $Fe_{10}Cu_{90}$, it was not possible to apply the same detailed analysis as for sample $Fe_{10}Cu_{90}$.

The Mössbauer spectrum of an Fe-poor sample ($Fe_{20}Cu_{80}$) was recorded at room temperature (see Figure 4). A non magnetic spectrum was observed, in agreement with superparamagnetic behaviour. This is consistent with the results derived above in $Fe_{10}Cu_{90}$, from magnetization measurements. It confirms the presence of Fe clusters in these alloys. Note that the observed isomer shift found is characteristic of fcc Fe-Cu alloys.

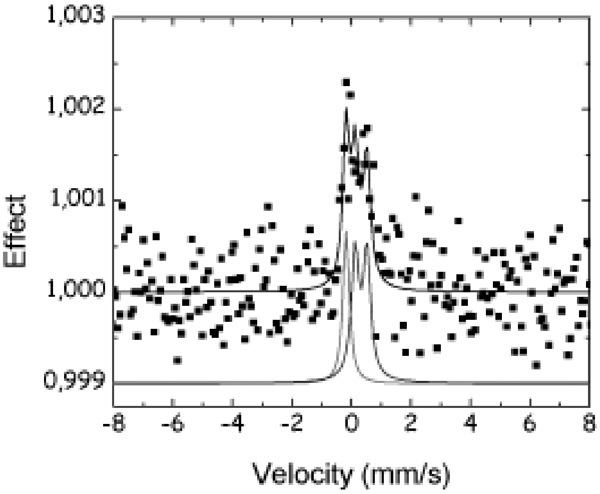

FIG. 4: Mössbauer spectrum at room temperature for a $Fe_{20}Cu_{80}$ alloy

V. ANALYSIS

The presence of Fe clusters in the present Fe-Cu alloys may naturally be associated with the immiscibility of the constituting elements, Fe and Cu. It indicates that, at the deposition temperature, the atoms keep sufficient mobility to assemble and reach a state of lower energy than in the metastable alloyed state.

We focus on the $Fe_{10}Cu_{90}$ alloy. The predominance of inter-cluster positive interactions leads us to propose that the clusters orders ferromagnetically below the paramagnetic Curie temperature of 160 K. However the spontaneous magnetization is significantly lower than the magnetization obtained at saturation (see Figure 1). Due to the expected heterogenous nature of the magnetization in these materials it may be suggested that long-range dipolar interactions manifest themselves at the scale of groups of clusters, leading to the formation of non-collinear magnetic arrangements.

In a system of magnetic particles diluted in an essentially non-magnetic matrix, the magnetic interactions (dipolar, RKKY, etc$\cdots$), are usually distributed about the value 0. They tend to stabilize cluster glass low-T moment arrangements with no bulk resulting magnetization. The existence of ferromagnetic order in a cluster assembly is termed superferromagnetism [10]. It implies that positive exchange interactions dominate other interactions [11]. Superferromagnetism has been found essentially in systems made of insulating matrices. In the present metallic system, (weak) intercluster exchange-coupling may a priori occur (i) via isolated Fe atoms within the Cu matrix or/and (ii) via direct local contact between clusters. Below the percolation limit, exchange via direct contact may only lead to the formation of finite-size ferromagnetic domains encompassing several clusters. Thus the observed formation of an infinite cluster suggests that isolated Fe atoms are present within the Cu matrix. Note that the transition from superferromagnetism to normal ferromagnetism occurs around $x = 30$, close to the percolation limit ($x = 28$). This suggests that as soon as clusters become in contact, strong inter-cluster exchange interactions develop, of which strength is of the same order of magnitude as intracluster interactions.

In previous studies, the properties of Fe-Cu alloys in the as-deposited state were discussed assuming that the Fe atoms were homogeneously distributed within the matrix [5,6,8,9]. Only after annealing, Fe clusters were found to occur. In the present system, the presence of clusters in the as-prepared alloys may be tentatively attributed to the pulsed electrodeposition procedure used. The instantaneous deposition rate of each given element is very high and due to their respective immiscibility, cluster formation is favoured.

VI. CONCLUSION

In Fe-Cu metastable alloys prepared by pulsed electrodeposition, it was shown that Fe clusters form directly within a non-magnetic Cu matrix. The clusters were shown to contain around 140 Fe atoms and to be superparamagnetic at room temperature. Below 160 K it was suggested that the clusters order into a superferromagnetic arrangement. This original behaviour was attributed to the persistence of weak exchange interactions mediated by isolated Fe atoms dispersed within the Cu non-magnetic matrix. Domain observation using low temperature MFM could help in establishing unambiguously the nature of the magnetic order in these materials.

Superferromagnetic materials may show very large magnetic susceptibility and it has been suggested that they could be used in applications where high magnetic permeability is needed [17]. This includes microelectronics devices (e.g small inductances) and micro-sensors.

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