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Citation: J. Appl. Phys. **76**, 6676 (1994); doi: 10.1063/1.358165
View online: http://dx.doi.org/10.1063/1.358165
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v76/i10
Published by the American Institute of Physics.

Magnetic properties of nanostructured thin films of transition metal obtained by low energy cluster beam deposition

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Clusters of iron, cobalt, and nickel are produced in a laser vaporization source. The size distributions of the incident clusters are checked by time-of-flight mass spectrometry before deposition at low energy. Studying the near threshold photoionization, Co_n and Ni_n clusters exhibit an icosahedral structure while for iron, no clear structure emerges. Neutral clusters were deposited on different substrates at room temperature with thicknesses up to 100 nm in view to determine their structure and magnetic properties. A limited coalescence of the clusters is observed from high-resolution transmission electron microscopy. No icosahedron has been observed but cuboctahedron and interface twins between adjacent particles have been clearly identified in Ni films. Grazing incidence x-ray diffraction experiments reveal a classical phase with grain size around 6 and 4 nm for Fe and Ni films, respectively but an anomalous fcc phase for Co films and a very low grain size of 2 nm. The density of films determined by x-ray reflectivity was estimated to represent only 60%–65% of the bulk density. Magnetic behaviors studied by ferromagnetic resonance and SQUID magnetization measurements have been interpreted using the correlated spin glass model. Mössbauer spectra performed on Fe films at zero field revealed the presence of 20% of iron in the form of thin nonmagnetic oxide skin surrounding Fe grains which allow to find 2.2 μB per magnetic iron atom in agreement with macroscopic magnetic measurements. Nevertheless we found an anomalous reduced atomic moment for Ni film.

INTRODUCTION

Recently, magnetic properties such as exchange coupling or giant magnetoresistance mainly observed in metallic multilayers have been detected in other nanostructured systems. For example, Berkowitz *et al.*[1] and Xiao *et al.*[2] observed giant magnetoresistances in ultrafine Co-rich precipitate particles in a Cu-rich matrix. These samples were prepared by coevaporation taking advantage of the low solubility of Cu in Co. However, though this technique is limited to nonmiscible components, the adjustable cluster diameter is a new parameter in addition to the distance between particles as in thin film layers. Thus, studies on clusters and cluster assembled materials are of increasing interest.

The laser vaporization source of the laboratory[3] allows the obtention of an intense cluster beam of any size distribution (from few to a thousand atoms per cluster) and the synthesis of cluster assembled materials, even of the most refractory and of the most complex ones. The cluster size distribution is checked by time-of-flight mass spectrometry before deposition. Our source producing cold clusters with low kinetic energy, incident clusters do not fragment on the substrate and may conserve their intrinsic structures. Thus we succeeded in the stabilization of very small size fullerenes (C_{20}-C_{32}), never previously observed experimentally. We clearly evidenced that deposited carbon clusters presented the in flight-clusters fingerprint.[3]

Our challenge in depositing transition metal clusters is to synthesize new phases where the anomalous crystallographic structures of free clusters would be kept and to study the specific magnetic behavior of these weakly correlated entities on a substrate. Once more, we show that our technique leads to a random compact cluster stacking (RCCS).[3] Thus magnetic results could be interpreted by random anisotropy model with a scale law and in terms of localization of spin waves.

EXPERIMENT

Our cluster source is based on the technique of laser vaporization.[3–5] Roughly, a plasma is created in a vacuum cavity by Nd-YAG laser light. Synchronized with the laser, a high pressure (5 bars) helium pulse, injected in the cavity by a nozzle, thermalizes the plasma and cluster growth occurs. The nascent clusters are then rapidly quenched during the following isentropic expansion into vacuum (10^{-7} Torr).

Cluster size distributions are analyzed in a time-of-flight mass spectrometer. Studying the near threshold photoionization (performed with a frequency-doubled tunable dye laser pumped by a XeCl excimer laser), mass spectra of Co_n and Ni_n clusters exhibit oscillations and a series of magic numbers ($n=13,55,147,309,561,\ldots$) corresponding to an icosahedral or cuboctahedral atomic shell structure in the obtained mass range (50–800 atoms per cluster). A finer analy-

 0021-8979/94/76(10)/6676/3/$6.00

sis allows us to conclude for the icosahedral structure.[6] For iron clusters, the results are not so simple, indicating a competition between different regimes.[6]

Then, free neutral clusters are deposited with a kinetic energy in the 10–20 eV range on different substrates at room temperature with thicknesses up to 100 nm in view to determine their structure and magnetic properties.

SAMPLE CHARACTERIZATION

The typical size of supported clusters obtained from high-resolution transmission electron microscopy (HRTEM) was about 2–6 nm for an initial size distribution centered around 150 atoms for Fe and 300 atoms for Co and Ni clusters, respectively. No icosahedron was observed but cuboctahedra and interface twins between adjacent particles was clearly identified in Ni films. Quasispherical grain morphology existed in Fe film which could correspond to a bcc rhombic dodecahedron [110] according to the Wulff's theorem.[7] Grazing incidence x-ray diffraction (GIXD) experiments exhibit a classical bcc phase for Fe films but a fcc phase for both Co and Ni with a grain size extracted from the peak width of about 6, 4, and 1.5 nm, respectively, in agreement with electronic diffractions and TEM observations. The classical structure of cobalt being hcp, the fcc phase observed in Co films might be related to the icosahedral structure of the incident cluster beam. In fact, the icosahedron is expected to be the precursor of the fcc crystal. The small grain size and the reminiscence of a free cluster structure confirm the limited coalescence process due to a weak diffusion of metallic clusters on the substrate even at room temperature.

Rutherford backscattering spectroscopy showed that these porous films are composed of 20%–30% of oxygen for 70%–80% of metals. The density of the films, determined by x-ray scattering at very low angle in $\theta/2\theta$ mode and from rocking curve around the critical angle of the total reflectivity, was estimated to represent only 60%–65% of the bulk density.[8]

MAGNETIC PROPERTIES

Mössbauer spectra performed at room temperature on Fe films without magnetic field revealed the presence of the sextet of the metallic iron (with hyperfine field around 332 KOe and representing 80% of the signal) and of two doublets corresponding to 20% of ferric oxide (Fig. 1). Whereas the common isomer shift of both nonmagnetic signals is equal to 0.4 mm/s compared to the metallic iron, the quadrupolar splittings respectively equal to 0.9 and 2.4 mm/s allow us to differ two types of oxide. The first one is identified as a thin layer of nonstoechiometric Fe_3O_4 or/and a mixture of stoechiometric Fe_3O_4 and γ-Fe_2O_3 phases[9] (in agreement with the GIXD experiments on the most oxidized films[10]). The second one, not identified so far could be related to a free-cluster oxidation. These results allow to describe the supported clusters as pure iron core surrounded by a thin skin (2 or 3 monolayers[7]) of non-magnetic oxide. On the other hand, the intensity ratio of the sextuplet (321123) evidences a random spatial distribution of the magnetization at zero field.

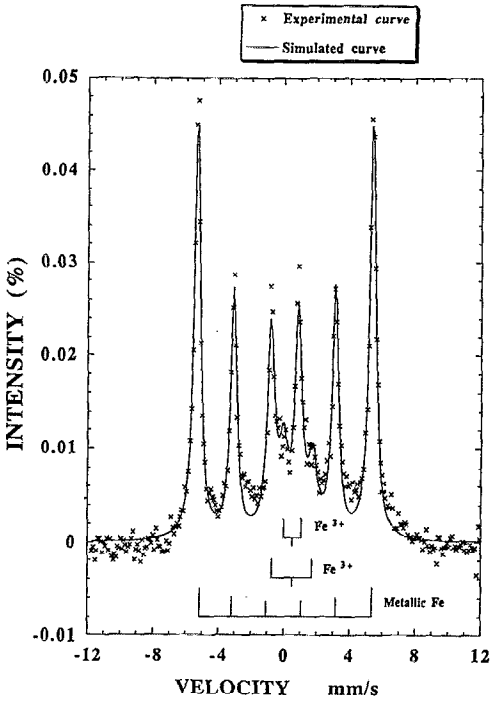

FIG. 1. Mössbauer spectra obtained on a Fe_{150} film at 300 K.

The macroscopic magnetic behavior of our films has been studied using ferromagnetic resonance (FMR) and magnetization measurements (SQUID). FMR curves roughly traduced a thin film behavior[11] but revealed several resonance magnetic fields due to anchorage of spin waves at the surface (when the applied field is perpendicular to the surface of the film). The coercive field at 300 K is about 100 Oe for cobalt, 50 Oe for iron, and lower than 10 Oe for nickel and increases at 10 K up to 1000 and 500 Oe for Co and Fe films, respectively. The value of the saturation magnetization was related to the density value and to the quantities of oxides. For iron in agreement with Mössbauer results, the classical atomic moment of 2.2 μB per magnetic iron atom is retrieved. On the contrary we found a strongly reduced value in Ni film. The atomic moment per Ni atom has been estimated to be equal to 1/4 of the bulk value (taking into account the film density). By extrapolating the magnetization curve versus temperature, the Curie temperature T_c has been found to be around 350–400 K. Thus the magnetization reduction can not be uniform, otherwise T_c would be much more reduced. This could be due to the presence of dead magnetic layers similar to that observed in Fe films and/or to antiferromagnetic coupling between Ni particles via Ni shell. Magnetoresistance measurements and magnetization under high magnetic field are in progress in view to see respectively an important negative magnetoresistance and a second transition of the saturation magnetization.

We fitted the approach to saturation of the magnetization using the Chudnovsky model.[12,13] The experimental law of approach to saturation in magnetic systems is perfectly fitted by the formalism of the random-anisotropy amorphous magnets. In the Chudnovsky's model,[12] a physical parameter is defined

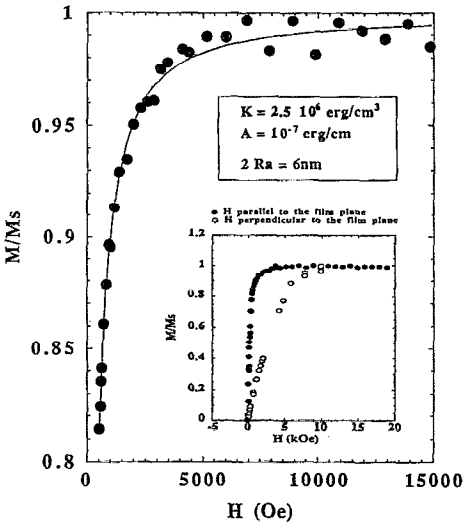

FIG. 2. Magnetization law in approaching saturation obtained on a Fe_{150} film at 300 K.

$$\lambda=\left(\frac{2}{15}\right)^{1/2}\frac{KR_a^2}{A},$$

where R_a is the distance over which the local anisotropy axes are correlated and A is the exchange constant. The parameter λ is the critical boundary between the correlated spin glass (CSG) regime ($\lambda<1$) and the speromagnetic state ($\lambda>1$). One can define the ferromagnetic correlation length $R_f=R_a/\lambda^2$. The best fit[10,13] of the curve on Fe films (Fig. 2) gives respectively, $2R_a=6$ nm, $K\sim 2.5 10^6$ erg/cm^3 (in agreement with FMR fits, to compare to 5×10^5 erg/cm^3 in the bulk), $A\sim 10^{-7}$ erg/cm, therefore $\lambda=0.66$ and $R_f=8$ nm. Let us underline that in amorphous alloys, R_a is always of the order of the inter-reticular distance (e.g., in rare earth-Fe compounds $R_a=0.5$ nm[14].) In our case we note that R_a exactly corresponds to the supported particles size and that the R_f value shows the ferromagnetic correlation limited to the first neighbors. However, if the ferromagnetic domain was strictly limited to the R_f value, the film should be superparamagnetic. That confirms the definition of R_f in the CSG model where it represents an exponential decay coupling. We thus showed that RCCS films can be described as an amorphous with an adjustable parameter R_a. In our case, R_a is great enough to reach experimental fields larger than the crossover field[11] $H_{co}=2A/M_sR_a^2$ which separates the region with and without random anisotropy fluctuations (determined around 3 kOe in Fe films). In Ni films (Fig. 3) we clearly see two regimes for the low field ($\Delta M/M_s$) variation versus temperature (maybe correlated to a $T_{\text{Néel}}$ of Ni oxide). At low temperature the random anisotropy fluctuations dominate (with a H^{-2} law) whereas at high temperature the exchanges dominate (with a $H^{-1/2}$ law), the transition occurring around 200 K.

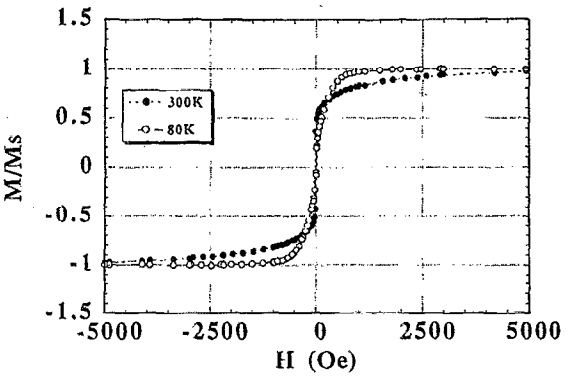

FIG. 3. Magnetization vs temperature obtained on a Ni_{300} film.

In conclusion, these first results lead us to pursue this study to elucidate some other characteristic magnetic parameters of the layers (T_c, e.g., antiferromagnetic coupling in Ni films, and complete magnetic study on promising Co films). In particular, x-ray absorption measurements will allow us to locally describe crystallographic and magnetic atomic environment in view to explain the anomalous atomic moment in Ni films. Experiments with cooled substrates are in progress to attempt to stabilize the icosahedral structure which is expected to lead to specific magnetic properties.

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