Giant magnetoresistance in Co-Ag granular films prepared by low-energy cluster beam deposition

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In this paper, we report on structural, magnetic, and magnetoresistive properties of Co-Ag granular films made by low-energy cluster beam deposition (LECBD). With this technique, we can grow granular films of cobalt clusters embedded in silver or other matrix materials, with independent control of the size and concentration of the clusters. Moreover, we show, from TEM, grazing-incidence small-angle x-ray diffraction, and magnetic measurements, that the size of the clusters is the same, whatever the matrix. We measured the giant magnetoresistance (GMR) and magnetic properties of cobalt clusters in silver, and found them similar to those of granular alloys made by codeposition of atoms. Then, taking advantage of the independent control on the size and distribution of the clusters allowed with LECBD, we studied the concentration dependence of the GMR. Its variation at low cobalt content seems to indicate that GMR in the granular geometry is intermediate between CIP and CPP. [S0163-1829(97)05605-1]

I. INTRODUCTION

Giant magnetoresistance (GMR) has been observed in magnetic multilayers[1] and then, recently, in granular films composed of magnetic clusters embedded in a nonmagnetic metal.[2] In both systems, multilayered and granular structures, the GMR is ascribed to similar processes of spin-dependent scattering.[3–5] The geometrical parameters defining the system, which are the layer thickness in multilayers, become the cluster size and intercluster distances (or clusters concentration) in the granular systems. Zhang and Levy[4] have shown that, at least if the spin-flip scattering can be ignored, the granular systems are self-averaging, which allows for deriving relatively simple expressions to calculate the GMR as a function of the cluster size and concentration.

However, a difficult problem for the interpretation of experimental results in granular systems is that, generally, the concentration (or, equivalently, the intercluster distances) and the size of the clusters cannot be chosen independently. It is thus difficult to separate the respective influences of sizes and intercluster distances, and to compare the experimental results with theoretical predictions.[4]

In this paper, we present results obtained with Co-Ag films prepared by low-energy cluster beam deposition (LECBD). With this technique, neutral clusters are produced in an inert gas condensation source and deposited at very low energy on a substrate.[6–9] In addition, for the work presented here, the LECBD of cobalt clusters is combined with deposition of silver atoms from a thermal evaporation cell, in order to bury the Co clusters in a Ag film. Moreover, the clusters deposited at very low energy do not fragment upon impact on the substrate, and the codeposition with silver limits their diffusion and coalescence, so that narrow size distributions can be obtained. On the other hand, the cluster concentration in the film is adjusted independently from the ratio of the cobalt cluster and silver deposition rates.

We have studied series of samples with approximately the same size of cobalt clusters—around 3 nm—and with volume concentration of cobalt varying between 3–50 %. This allows us to investigate how the GMR depends on the intercluster distances and, at the highest concentrations, on the magnetic interactions between clusters.

II. SAMPLE PREPARATION AND STRUCTURAL CHARACTERIZATION

The cobalt clusters are produced by a laser vaporization source. This source, described in detail elsewhere,[6] uses a pulsed YAG laser (wavelength, 532 nm, repetition rate, 30 Hz) for the ablation of an ultrahigh purity cobalt rod. Synchronized with the laser pulses, high-pressure helium gas pulses (~5 bars) are injected into the source to cool the plasma generated at the surface of the rod and nucleate clusters. Those clusters are subsequently completely cooled and

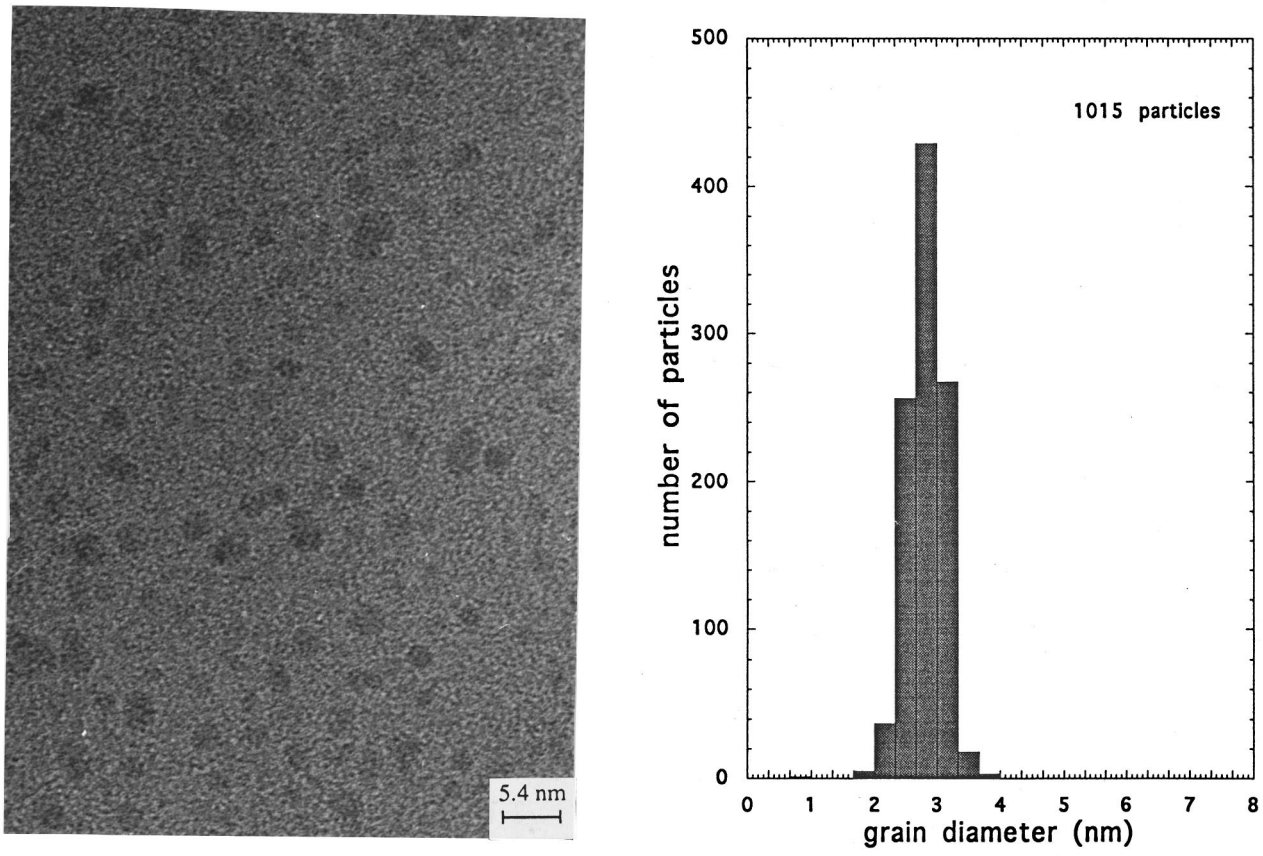

FIG. 1. TEM image of a thin film (~15 nm) of cobalt clusters embedded in a SiO_x matrix. The film was prepared by codeposition at room temperature on an amorphous carbon coated grid of neutral Co clusters jet (mean size centered around Co_{300}) produced in the laser vaporization source and thermally evaporated SiO_x. The atomic concentration of cobalt is about 10%. In this concentration regime (below the percolation threshold, measured around 25 at. % cobalt, see section II), we observe isolated Co nanograins with a relatively narrow size distribution centered around 3 nm diameter, as shown in the inset.

stabilized in the supersonic expansion which takes place at the exit of the source, in a vacuum chamber ($\sim 10^{-6}$ Torr).

A high-resolution time-of-flight mass spectrometer in the reflectron geometry is mounted perpendicularly to the cluster jet direction, at the exit of the cluster source. This spectrometer is used to characterize ionized clusters directly from the source, or clusters photoionized by a UV tunable laser. The size distribution is generally Gaussian and centered around a mean size that depends on the experimental parameters (laser intensity, gas pulse pressure, geometry of the nucleation chamber and nozzle, etc.). The neutral cobalt clusters are deposited on various substrates, at room temperature in a deposition chamber in line with the source. Their energy is the very low energy gained in the supersonic expansion at the exit of the source. A thermal evaporation cell located in the deposition chamber allows us to bury the clusters in various matrices (silver, silicon oxide, etc.). The cluster concentration in the resulting film is adjusted from the ratio of the cluster and matrix deposition rates, as measured with an oscillating quartz balance. With this technique, the mean size of the embedded clusters is controlled from the gas phase and the deposition conditions, and is thus independent from their concentration in the film. This is in contrast with granular systems prepared by precipitation or codeposition, where the particle size and concentration are dependent.

In Fig. 1, we show an example of a transmission electron microscopy (TEM) image of a SiO_x film (deposited on an amorphous carbon coated grid) with 10% of embedded Co clusters. This TEM picture reveals nearly spherical fcc cobalt grains with a narrow size distribution around 3 nm in diameter (inset). The size distribution determined from TEM changes only slightly with the clusters concentration, at least for concentrations below 15%. We could not obtain similar TEM characterizations for Co clusters in Ag. However, as presented in the next section, we have found that the superparamagnetic blocking temperatures are practically the same for clusters embedded in Ag or SiO_x with the same concentrations. Consequently, we can suppose that the size distribution is only weakly affected by the matrix and assume that the size distribution in Ag is approximately the same as the one derived from TEM in SiO_x films with the same cobalt content. It is not surprising to obtain comparable size distributions in different matrices, since, with our deposition technique, the size distribution is mainly governed by the sizes in the beam, with only weak effects from diffusion and coalescence on the substrate.

Due to percolation, TEM characterization becomes difficult for volume concentrations of clusters above 20%. This also corresponds to the range where electrical percolation sets in in samples with SiO_x matrices, resulting in a more complex morphology of the granular structure. However, grazing-incidence–small-angle-x-ray-diffraction (GISAXD) performed with synchrotron radiation still indicates homogeneity length around 3 nm. This suggests a structure with

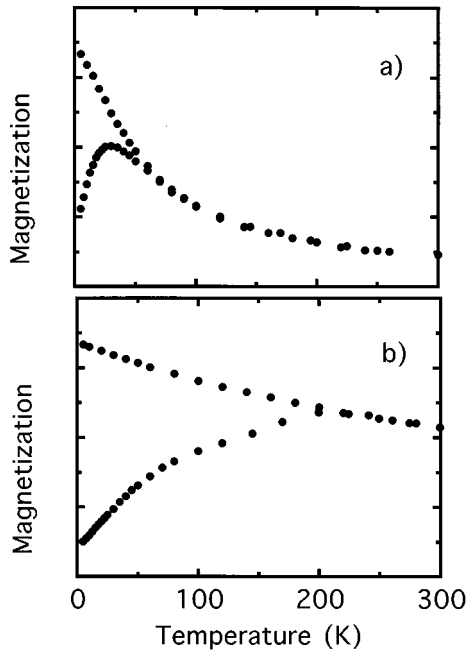

FIG. 2. FC and ZFC magnetization curves in 100 Oe for Co clusters embedded in Ag with volume concentration of 7% (a) and 23% (b).

chains of interconnected small grains in the highly concentrated films.

An independent determination of the cluster sizes comes from the analysis of the field dependence of the magnetoresistance, as explained in Sec. III. Again, this determination is quantitative only in the low concentration limit where the clusters are magnetically uncoupled and thus present a typical superparamagnetic behavior. We will see in Sec. IV that the size determination from GMR agrees approximately with that from TEM.

III. MAGNETIC PROPERTIES

We have performed magnetization measurements on field-cooled (FC) and zero-field-cooled (ZFC) samples to characterize the superparamagnetic behavior of the cobalt clusters. In Fig. 2, we show the temperature dependence of the FC and ZFC magnetization, in 100 Oe, for two concentrations.

In diluted samples, with volume concentration below 15%, we find the typical superparamagnetic behavior, as in Fig. 2(a). The average blocking temperature T_b can be defined from the maximum of the ZFC curves, and it shows some increase when the concentration of cobalt clusters increases. In Fig. 3, we have plotted the blocking temperatures as a function of the cobalt concentrations for cobalt clusters in silver and for cobalt clusters prepared in the same conditions, but embedded in silicon oxide. The blocking temperature in Ag and SiO_x are very similar, which indicates that the cluster size distribution is approximately the same in both matrices. We can therefore suppose that the size distribution determined from TEM for a given cobalt clusters concentration in SiO_x also holds for cobalt clusters in silver. This will be confirmed by our analysis of the magnetic field dependence of the GMR, which provides an independent determination of the size distribution. A third determination of the sizes can be obtained, for the very low cobalt concentrations, from the Curie-Weiss constant of the superparamagnetic behavior above T_b. For example, we have derived for the sample with 7% Co clusters [Fig. 2(a)], an average diameter of 2.7 nm, in approximate agreement with the data of Fig. 1.

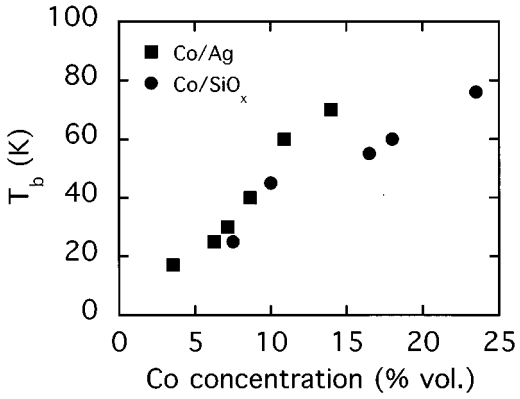

FIG. 3. Blocking temperature vs volume concentration for Co clusters deposited in the same conditions but embedded in Ag (squares) or SiO_x (circles).

For volume concentrations larger than about 15%, the blocking temperature increases rapidly and the FC-ZFC curves depart markedly from a typical superparamagnetic behavior, as can be seen in Fig. 2(b). This is probably due to the progressive crossover to a ferromagnetic system of interacting, coupled clusters. This is also confirmed by the reduction of the GMR in the concentrated samples, as discussed in the next section.

Finally, in Fig. 4, we present examples of magnetization cycles below and above the blocking temperature for a film with 7% of cobalt clusters. Below the blocking temperature [Fig. 4(a)], the magnetization curve is irreversible with a coercive field of about 400 Oe. Above T_b [Fig. 4(b)], we observe almost reversible magnetization curves and high saturation, as expected for a superparamagnetic system.

IV. MAGNETORESISTANCE

Figure 5 shows the GMR of the Co-Ag granular systems measured at 5 T, for different volume concentrations. The

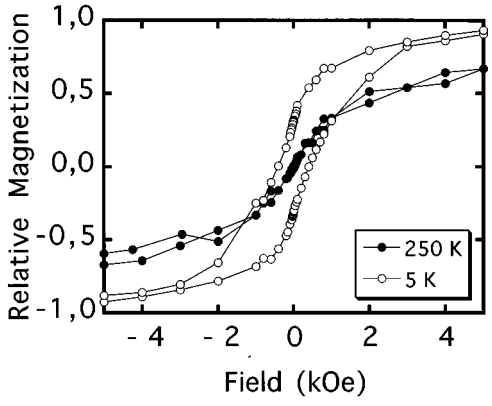

FIG. 4. Magnetization cycles for a film with a volume concentration of Co of 7%: 5 K, below T_b (open dots) and 250 K, above T_b (closed dots).

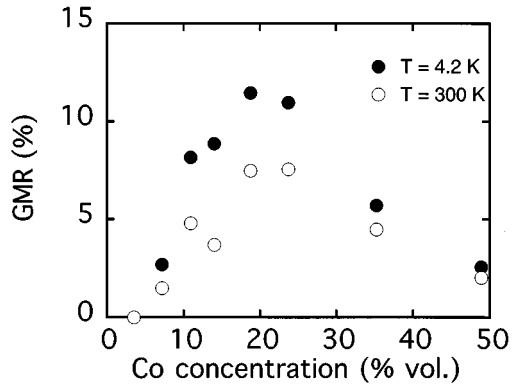

FIG. 5. Giant magnetoresistance in Co-Ag films, as a function of the Co volume concentration, measured at 4.2 K (closed dots), and room temperature (open dots).

GMR effect increases as the cluster concentration increases, and reaches a maximum (12% GMR) at $T=4.2$ K for 19% Co. For higher concentrations, the GMR decreases with the onset of direct magnetic coupling between the cobalt particles (as confirmed by the observed crossover from superparamagnetic to magnetically ordered behavior).

In granular systems, the state where the moments of magnetic clusters are random (at the coercive field H_c) has a larger resistance than the state where the moments are aligned by an external field. Figure 6(a) shows the GMR of the Co_7Ag_{93} at $T=4.2$ K. We also show in Fig. 6(b) the hysteresis loop of Co_7Ag_{93} which closely correlates with the magnetoresistance curve. As has been pointed out by Gittleman, Goldstein, and Bozowski,[10] the magnetoresistance can be expressed as $A(M/M_s)^2$, where M_s is the saturation magnetization and A the negative amplitude of the GMR. We show in Fig. 7(b) the magnetization curve for the same sample, and the correlation between the GMR and the square of the magnetization can be seen from Fig. 7(a), where $A(M/M_s)^2$ appears as a full line. Apart from deviations at high field, the agreement between the two curves is very good. In fact, when the magnetization approaches saturation, deviations of GMR from M^2 are quite significant, because the most important contribution to the magnetoresistance comes from smaller superparamagnetic clusters while their contribution to the total magnetization is small.

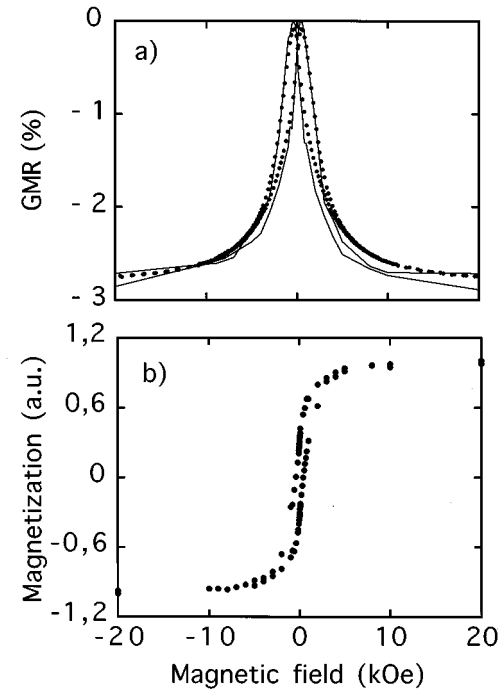

FIG. 6. (a) Giant magnetoresistance in Co_7Ag_{93} films, measured at 4.2 K, as a function of the applied field (closed dots); (b) magnetization as a function of the applied field for the same film and temperature. In panel (a), the full line is the square of the magnetization.

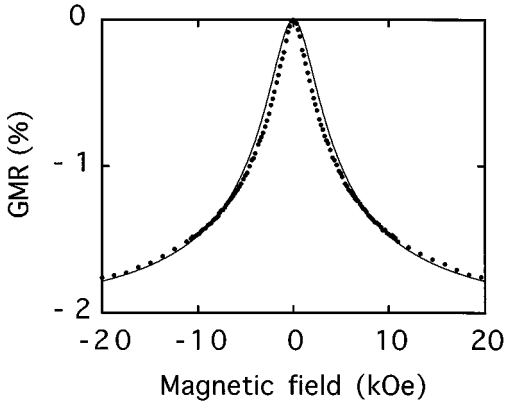

FIG. 7. Giant magnetoresistance in Co_7Ag_{93} films, measured at 100 K, as a function of the applied field (closed dots). The full line is a fit to the data, using Eq. (2), with $p_s=0.31$, $\lambda_{Co}=30$ Å, $\lambda_{Ag}=150$ Å, and $\lambda_s=6/a_0$, and cluster size distribution centered on 2.4 nm.

In magnetic multilayers, the GMR effect is enhanced when the current is perpendicular to the plane of the layers (CPP geometry). In granular systems, the current is neither parallel nor perpendicular to the magnetic cluster surfaces, giving a slightly different picture for the GMR. However, Zhang and Levy[4] have argued that the problem of the GMR in granular systems should be similar to that of the CPP case, with self-averaging of the scattering. With this self-averaging assumption, the GMR can be written as

$$\mathrm{GMR}=\frac{\Delta\rho}{\rho(H_c)}=\frac{\xi_1^2}{\xi_0^2}, \tag{1}$$

$$\xi_0=\frac{1-c}{\lambda_{nm}}+\frac{c}{\lambda_m}+\frac{(36\pi)^{1/3}c(1+p_s^2)}{\lambda_s/a_0}\,\frac{\int V_\alpha^{2/3}f(V_\alpha)dV_\alpha}{\int V_\alpha f(V_\alpha)dV_\alpha}, \tag{2a}$$

$$\xi_1=\frac{2cp_b}{\lambda_m}\,\frac{\int V_\alpha f(V_\alpha)m_\alpha(V_\alpha)dV_\alpha}{\int V_\alpha f(V_\alpha)dV_\alpha} + \frac{2(36\pi)^{1/3}cp_s}{\lambda_s/a_0}\,\frac{\int V_\alpha^{2/3}f(V_\alpha)m_\alpha(V_\alpha)dV_\alpha}{\int V_\alpha f(V_\alpha)dV_\alpha}, \tag{2b}$$

where c is the clusters volume concentration; a_0 is the lattice constant of the magnetic clusters; $m_\alpha(v_\alpha)$ is the component of the magnetization of the αth particle along the applied field; $f(v)$ is the distribution function for the size of the

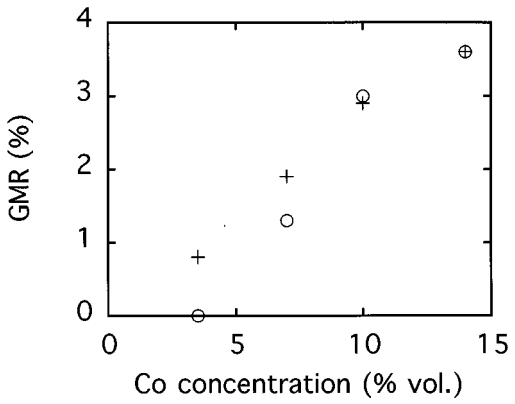

FIG. 8. Measured giant magnetoresistance in films with low Co content (open dots), and expected values from the fit using the same set of scattering and mean-free-path parameters as for the sample with 14% Co (crosses).

magnetic particles; λ_{nm} and λ_m are the mean free paths within the matrix and within the cobalt particles, respectively; λ_s is the mean free path at the interfaces; and the ratio of spin-dependent to spin-independent scattering potentials within the magnetic clusters is p_0, and at the interfaces is p_s.

Using previous results, it is possible to reduce the number of free parameters involved in the calculation of the GMR. First, in Co/Ag multilayers, previous works suggest that spin-dependent scattering occurs primarily at the precipitate-matrix interface. In granular Co-Ag systems, the surface to volume ratio is three times more important than what is found in equivalent multilayers systems (when the thickness of the magnetic layers is equal to the cluster diameter). So, we can therefore assume that the bulk contribution term—proportional to p_b—is zero. An example of fit—for Co_7Ag_{93} at 100 K—is shown in Fig. 7. The fit is obtained with $p_s=0.31$, $\lambda_{Co}=30$ Å, $\lambda_{Ag}=150$ Å, $\lambda_s=6/a_0$, 2.4 nm for the mean diameter and 0.4 nm for the width of the diameter Gaussian distribution. The field dependence of the GMR is controlled by only the size (mean diameter and distribution width), while the parameters p_s, λ_{Co}, λ_{Ag}, and λ_s govern its amplitude. The parameters giving the best fit change slightly with the concentration of Co. For example, at 14% Co, the best fit is obtained with the same values for λ_{Co}, λ_{Ag}, λ_s and for the size distribution width, but with a mean diameter of 3.3 nm and $p_s=0.34$. The moderate variation of the diameter with the concentration is consistent with the concentration dependence of the blocking temperature. To explain the variation of p_s with the concentration, we cannot rule out some concentration dependence of the structure of the interface or concentration of defects. An alternative explanation is that the self-averaging model of Zhang and Levy is less applicable at low concentrations. We show in Fig. 8 the concentration dependence of the GMR ratio calculated with a constant value of p_s, that is, the one found for 14% Co. The experimental values depart downward for the calculated curve at low concentrations, which could reflect a partial breakdown of the self-averaging hypothesis in this concentration range. Measurements at lower concentration could be useful to establish more clearly such deviation.

Finally, we would like to emphasize that this study would have been impossible to carry out without the use of LECBD, because, contrary to usual codeposition techniques, it allows independent control on the size and concentration of the clusters in the granular alloys.

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