Improved giant magnetoresistance in nanogranular Co/Ag: The role of interparticle RKKY interactions


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A record 40% room temperature giant magnetoresistance has been achieved in a nanogranular Co/Ag alloy by optimizing the concentration, sputtering conditions, and cumulative short thermal treatments. Upon annealing, the giant magnetoresistance effect exhibits a local minimum at 230 °C before reaching its maximum at 300 °C. Assuming the presence of both dipolar and RKKY-like exchange interactions between the particles, these features can be accounted for by considering that the latter correlations are progressively inhibited as the matrix, a supersaturated Ag-Co solid solution, segregates the solute Co atoms. This idea is supported by the temperature dependence of the magnetization in samples submitted to different annealings, where the zero-field cooled magnetization peaks at the lowest temperature in the sample exhibiting the largest magnetoresistance effect.

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I. INTRODUCTION

In 1992, Berkowitz et al.1 and Xiao et al.2 independently reported the discovery of giant magnetoresistance (GMR) in Co/Cu nanogranular samples. The GMR effect had been observed a few years ago in magnetic multilayers with an antiferromagnetically coupled sublattice.3 In both types of nanoscale systems, the GMR arises from spin-dependent electron scattering,4,5 yielding a reduced resistivity when the magnetic layers/nanoparticles are aligned. Shortly after its discovery, a similar GMR effect was reported for various granular systems, the most intense one being observed in the Co/Ag system,6–12 the subject of this article: Xiao et al. achieved a 24% GMR (at room temperature, RT, and 50 kOe applied field) in a 28% at. Co concentrated (20% vol.) sample grown on nitrogen-cooled substrates and subsequently annealed at 330 °C;5 Stearns and Cheng reported later a 31% GMR in a 37% at. Co concentrated sample,16 Co concentrated sample, grown on warm substrates, but this value was deduced after extrapolating the data to an infinite field (the effect amounts to about 20% at 15 kOe).12 A decade later these values still remain, to the best of our knowledge, the highest GMR found in a granular alloy in spite of the numerous studies on the impact of the geometrical parameters defining these systems—particle size and concentration6,7,9,11—intensive research on the effect of thermal treatments either in the form of warm substrates during the deposition or post-annealing of various types,7–9 and the use of advanced techniques such as preformed cluster deposition.6,11

Thermal treatments affect the GMR properties of sputtered and melt-spun immiscible alloys, since these nonequilibrium synthesis methods produce supersaturated solid solution matrices that will segregate the magnetic species upon annealing.13 Such variations have been mostly related to the growing particle size, or to changes in the quality of the particle/matrix interface,14 whereas little attention has been paid to the role of the matrix microstructure/composition,10 customarily thought to affect the GMR ratio only through its resistivity.12 However, in the context of spin-glass phenomenology in granular samples, López et al. have proved recently the important role of interparticle RKKY-like interactions enhanced by the presence of Co solute atoms in the matrix.16 In this work, we argue that correlations arising from this type of exchange interaction played a crucial role in the remarkable improvement of the GMR effect, up to 40% at RT and 15 kOe, obtained after carefully optimizing both the sputtering and annealing conditions. Cumulative short thermal treatments at increasingly high annealing temperatures provided us with the sensitivity needed to observe for the first time a minimum, preceding the usual peak, in the GMR evolution upon annealing. This new feature offers further support to the experimental findings of López et al. on the nature of interparticle RKKY-like interactions, whose existence17 and relevance versus dipolar interactions18,19 in systems with pure metallic matrices had been, in fact, discussed before in a few theoretical works.

II. EXPERIMENTAL

Ag$_{1-x}$Co$_x$ alloys were produced in the range 0.20$\leq x \leq 0.35$ by rf magnetron sputtering using a composite cathode consisting of high purity ($\approx 99.99\%$) small Co pieces symmetrically arranged on a silver target. Films with a final thickness close to 8 µm were grown on glass substrates at RT (in contrast with Xiao et al., who held the substrates at 77 K)2 at a deposition rate of 1.1 nm/s. The residual pressure was 4$\times 10^{-7}$ mbar, and the Ar pressure during deposition 3$\times 10^{-3}$ mbar. For each target configuration, various rf powers were employed in order to fine-tune the composition and thus optimize the GMR effect. Sample composition and homogeneity was checked employing an EDAX microprobe. Magnetization loops up to 15 kOe were recorded employing a commercial VSM magnetometer, which also provided the magnetic field for magneto-transport measurements (performed with the usual four-probe method). A Quantum Design SQUID magnetometer was used to measure the tem-
perature dependence of the magnetization in selected samples. Structural relaxation processes were tested with a Perkin-Elmer DSC (Differential Scanning Calorimeter). Finally, a Philips X′pert diffractometer was employed to record x-ray diffraction (XRD) patterns.

III. RESULTS AND DISCUSSION

As conventionally done, we define the magnetoresistance ratio (GMR) as $\Delta R/R_s = (R_{\text{max}} - R_{H=15 \text{ kOe}})/R_{H=15 \text{ kOe}}$, where $R_{\text{max}}$ is the zero-field resistivity, and $\Delta R_{m}=R_{\text{max}}-R_s$ the contribution to the resistivity due to spin-dependent electron scattering. The highest field available (15 kOe) was not enough to achieve complete saturation (see Fig. 2 later). Figure 1 shows the GMR concentration dependence in the as-deposited samples, among which the highest value was found for $x=0.29\pm0.01$ samples (Co volume fraction =21%) grown with a rf power of 70 W. This value for the optimum concentration agrees fairly well with previous experimental and theoretical reports. It is interesting to note in passing that, for this target configuration, higher rf powers provoked a pronounced decrease in GMR, probably due to the combined effect of the resulting slightly higher Co concentration and the higher mobility of the atoms, which leads to the formation of larger particles. In the following, we focus on this sample, Co$_{0.29}$Ag$_{0.71}$, and peer into the evolution upon annealing of the MR, $\Delta R_{m}$, $R_{\text{max}}$, the effective particle magnetic moment ($\mu$), and the coercive field ($H_C$).

The thermal treatments consisted of 20 min isothermal annealings at $T_{\text{ann}}$, which was reached from RT at 10 K/min, followed by a quench back to RT. Figure 2 shows the MR($H$) curves measured for the as-deposited sample and after annealing up to $T_{\text{ann}}=230^\circ C$ (minimum GMR), 298 $^\circ C$ (maximum GMR), and 395 $^\circ C$. For the sample showing the largest GMR, the inset shows as well the magnetoresistance measured at $T=5$ K.

For ideal superparamagnets, $M=M_s [\coth(x)-1/x]$, where $x=\mu H/\kappa_B T$, which yielded $\mu = 7140 \mu_B$ for the sample exhibiting the maximum GMR (see Fig. 3). This is the magnetic moment of a pure Co spherical particle with a 4.45 nm diameter. Although the fit is very good, it must be emphasized that this is a crude estimation for the particle moment, for the presence of a small but well-resolved hysteresis (see the inset in Fig. 3) proves that the superparamagnetic particles are not magnetically isolated, as the Langevin expression assumes. The coercive field for this sample, $H_C=6$ Oe, is the lowest one found during the annealing experiment, the significance of which will be addressed below. Dipolar interactions alone have been shown to produce, even in less concentrated particle systems, collective spin-glass-like dynamics at low temperatures when the particles are randomly dispersed. More specifically, Allia et al. have recently proved and justified that dipolar interactions in nanogranular alloys give rise to a slight magnetic hysteresis. Correlations originating from possible RKKY-like interactions may also produce hysteric...
behavior, as in spin glasses. Therefore, in this context, $H_C$ can be considered one more indicator of interparticle interactions.

Figure 4 shows the evolution upon annealing of the zero field resistance ($R_{\text{max}}$), the resistance related to magnetic scattering ($\Delta R_m$), the particle effective magnetic moment ($\mu$), and the coercive field ($H_C$), whereas the conventional GMR ratio is displayed in Fig. 5. The value of $R_{\text{max}}$ decreases markedly after $T_1 = 200$ °C—due to the onset of Co segregation out of the Ag matrix. All the features in Fig. 5 appear more sharply in the $\Delta R_m$ graph, where the $R_{\text{max}}$ variation has been filtered out. The decrease in $R_{\text{max}}$ does not lead to the expected increase in MR [since MR = $(R_{\text{max}} - R_0) / R_0 = \Delta R_m / (R_{\text{max}} - \Delta R_m)$], the reason being that the absolute magnetoresistance $\Delta R_m$ falls too. $T_1$ roughly coincides with a rise in $H_C$, which peaks at $T_2 = 230$ °C, noticeably the same temperature as the local minimum in $\Delta R_m$ (and MR). After $T_2$, the MR starts growing up to $T_3 = T_{\text{max}} = 298$ °C, which again coincides with the minimum in $H_C$. It is remarkable how accurately the three singular points in $\Delta R_m(T_{\text{ann}})$ are reflected in the coercive field. This, together with its small magnitude, reinforces our interpretation of the magnetic hysteresis as stemming from interparticle correlations, and not, as usually assumed in granular samples, from blocked particles. The Langevin-estimated magnetic moment increases monotonously after $T_1$, but grows much faster after $T_{\text{max}}$.

A maximum in GMR has been detected before, but not always, in annealing experiments on various granular systems—such as Fe/Ag, Co/Cu, and Co/Ag itself—but never following a local minimum. A possible reason might be the lack of an effective resolution in $T_{\text{ann}}$ (or annealing time) in many of those experiments. However, a word of caution must be said about the difficulty in comparing results for nanogranular systems, even with the same composition and synthesized with the same technique, since the fabrication parameters may affect the microstructure of the samples. In the Co/Cu alloy, where a relatively high homogeneity can be achieved by vapor quenching on cold substrates, the maximum has been explained in terms of progressive phase separation providing an optimum particle size and concentration before the particles start to coalesce at higher annealing temperatures. In the more immiscible Co/Ag system, Carey et al. realized that their maximum GMR upon annealing originated from the decrease of both $R_{\text{max}}$ due to the removal of structural disorder, and $\Delta R_m$, which is generally accepted to arise mainly from spin-dependent scattering at particle/matrix interfaces, whose den-
been subsequently used to help explain the Co atoms upon annealing. This interaction mechanism has a superparamagnetic scenario as the matrix segregated the magnetic phenomenology of their sample from a spin-glass-like transitions between the particles, to the extent of shifting the magnetic interactions in certain metallic nanogranular samples. These authors have convincingly shown in a rapidly quenched Co/Cu metastable alloy how the presence of atoms of the magnetic species dissolved in the matrix strongly enhances RKKY-like exchange interactions between the particles, to the extent of shifting the magnetic phenomenon of their sample from a spin-glass-like to a superparamagnetic scenario as the matrix segregated the Co atoms upon annealing. This interaction mechanism has been subsequently used to help explain the superspin-glass phase transitions exhibited by some heterogeneous granular systems. Keeping in mind this new contribution to the particle correlations, the following model for the Co atoms segregation consistently accounts for all the features of the data plotted in Fig. 4.

The diffusive flux of solute atoms from the matrix to the particles begins at $T_1$. At this point there is a relatively high concentration of Co atoms in solid solution with the Ag matrix. In fact, from the shift of the fcc Ag x-ray diffraction peaks (see Fig. 6), it is estimated that the silver matrix contains as much as 3% of Co in solid solution. Thus, in a first stage between $T_1$ and $T_2$, dipolar interactions increase as a result of the increasing particle size, whereas the RKKY-like exchange is not altered much—the Ag matrix not yet being sufficiently depleted of Co atoms as to inhibit it—and therefore one observes a decrease in MR and a rise in the coercive field. At $T_2$ the solute Co atoms in the Ag matrix reach the critical concentration so that further impoverishment will begin to inhibit RKKY interactions. Notice that the total Co atomic concentration in the granular Co/Cu sample studied in Ref. 16 was only 2.5%, only slightly higher than the estimated solute Co concentration in our sample (2.1%); this is consistent with the observation of a first stage in the annealing of Co$_{0.29}$Ag$_{0.71}$ without much effect on the intensity of solute Co-mediated RKKY interactions. The Co impoverishment of the matrix might not be a homogeneous effect, for the Co atoms closer to the particles are more likely to join them, with the subsequent formation of a Co-depleted shell that would enhance the inhibition of indirect exchange interactions. The MR increases $(H_C$ decreases) sharply, down to $H_C=6$ Oe at $T_{max}$, with the loss of magnetic correlations. Above $T_{max}$, the thermal energy supplied is high enough to enable the onset of coarsening, i.e., the coalescence of entire magnetic particles. Particle coarsening is clearly hinted at by the pronounced increase of the effective particle moment above $T_{max}$. The subsequent drastic reduction in particle density, and thus the density of particle/matrix interfaces, yields a rapid reduction in MR.

The progressive segregation of Co atoms out of the Ag matrix is clearly observed by x-ray diffraction in the relaxation of the fcc Ag reflections toward their bulk positions. This is illustrated in Fig. 6, which shows the variation upon annealing of the lattice parameter as calculated from each of the four peaks observed in all the diffraction patterns (for example, the pattern recorded for the as-deposited sample is shown in the inset). The matrix-nanogranules system is highly textured with the fcc [111] direction perpendicular to the surface. As the annealing temperature increases, the matrix and nanoparticle lattice parameters approach, respectively, the bulk fcc Ag and Co values, indicating the completion of phase separation. The occurrence of the two structural relaxation processes postulated above, Co segregation and particle coarsening is suggested too by the DSC scan measured for an as-deposited sample (Fig. 7). A very thick film (20 μm) was grown, and separated from the substrate, in order to provide enough sample mass for this experiment. The scan was taken upon heating at 10 K/min, and displays the onset of a first exothermic process at about 200 °C (Co segregation) and a second one at higher temperatures (particle coarsening). The onset temperatures for these largely

![FIG. 6. Variation upon annealing of the fcc matrix and nanoparticle lattice parameters as calculated from each of the four reflections appearing in the x-ray diffraction patterns [solid symbols are used for Co and empty ones for Ag, circles for (111) and squares for (222) reflections]. The inset shows, as an example, the pattern recorded in the as-deposited sample.](image)

![FIG. 7. The DSC scan, performed heating at 10 K/min, in as-deposited Co$_{0.29}$Ag$_{0.71}$.](image)
overlapping processes depend on the scan temperature rate. Besides, the thermal treatment to which the sample is submitted during the DSC scan is very different from that during the cumulative annealing experiment, and therefore one should not expect a full agreement with the onset temperatures of the structural changes suggested by the data in Fig. 4. Nonetheless, the DSC data helps to confirm that only two relaxation processes take place upon annealing this metastable sample.

In all the preceding discussion, we have tacitly assumed that the short range correlations between superparamagnetic particles introduced by both dipolar and RKKY interactions are ferromagnetically sensitive, since they reduce the magnetoresistance effect (due to the reduction of the zero-field magnetic disorder that provides its basis). In fact, short range ferromagnetic correlations, extending over a few particles, have been identified before by small angle neutron scattering in other dense granular thin films, and justified on the basis of an increasing electronic mean-free path, and on the basis that such systems are likely to contain regions that are approximately close-packed, which order ferromagnetically if the moments interact dipolarly. Concerning RKKY interactions, it has been suggested that they would increase too the effective domain size, but no rigorous prediction has been made yet on what type of magnetic ordering would result from interparticle RKKY interactions in concentrated metallic granular systems.

In order to further test our interpretation, which hinges on interparticle correlations, against others considering effects unrelated to the mutual orientation of the particles, such as variations in the interfacial roughness or in the electronic mean-free path, we have measured the FC and ZFC magnetization as a function of temperature in three representative samples: the as-deposited one, after annealing up to 298 °C (the sample exhibiting the maximum GMR, 40%, in the series), and after annealing up to 420 °C (well above the maximum). The results are plotted in Fig. 8. It is now well established that the low temperature magnetic state of a concentrated ensemble of randomly distributed nanoparticles is a collective one with similar properties to a spin-glass, the maximum in the ZFC not being any longer an individual blocking temperature, but a transition temperature determined by the strength of the interparticle interactions. Although the many studies leading to such a statement were performed mostly in frozen ferrofluids (only dipolar interactions between particles), the same is expected to be valid for RKKY interacting nanoparticles (canonical spin glasses have higher freezing transitions when the interaction between the atomic spins is stronger). Consistent with our explanation for the evolution of the GMR upon annealing, the lowest transition temperature is indeed observed in the sample exhibiting the maximum GMR. Notice that the data measured in the sample annealed up to 420 °C have been rescaled, since the signal includes a large background from coarse particles. It is a remarkable result that the ZFC maximum of a granular sample shifts to lower temperatures when the nanoparticles grow upon annealing, emphasizing the presence and importance of nondipolar interactions in the system depending more strongly on parameters other than the size of the particles. Allia et al., studying the GMR evolution upon Joule heating of rapidly solidified CoCu ribbons, found that the reduced magnetoresistance curves (MR vs $M/M_S$) became more parabolic (as in ideal superparamagnets) after some annealing, and rationalized this behavior in terms of an increasing electronic mean-free path (decreasing zero-field resistivity). These results can also be explained by the ideas presented here: the measurement of the ZFC magnetization being the test to elucidate their origin, at least in samples with a sufficiently high Co concentration. The as-deposited Co$_{29}$Ag$_{61}$ sample has a transition temperature beyond our available temperature range; we then repeated the annealing experiment in a less Co concentrated sample, Co$_{25}$Ag$_{75}$ (with 17% GMR as-deposited), and obtained the same result, this time with complete FC-ZFC curves: the thermal treatment optimizing the GMR (21%) leads to a much lower transition temperature in the ZFC magnetization (see Fig. 9). Finally, concerning the reproducibility of the data reported in this work, it must be remarked that all the features displayed by the data plotted in Fig. 4 were found in...
IV. CONCLUSIONS

In short, the optimization of composition, sputtering power, and thermal treatments has led to a record 40\% giant magnetoresistance in granular Co/Ag. The presence of new features in the evolution of the GMR and absolute magnetoresistance upon annealing (a minimum and a maximum, respectively) were explained postulating the presence of RKKY-like interparticle interactions enhanced by the Co atoms dissolved in the Ag-rich matrix, an idea supported, among other results, by the shift of the ZFC magnetization maximum toward lower temperatures. The GMR effect is optimized by thermal treatments yielding an efficient segregation of the Co solute atoms remaining in the Ag matrix, yet not severe enough to provoke any particle coarsening. The aggregation of Co atoms from the matrix to the nanoparticles increases their size and, therefore, their dipole-dipole interaction. However, it inhibits the RKKY-like interaction mechanism proposed in Ref. 16, yielding a more disordered zero-field magnetic configuration and therefore an enhanced magnetoresistance. This second factor determines the maximum GMR value attainable upon annealing.

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