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Giant magnetoresistance study of granular Co–Fe /Ag thin films: correlation with magnetization

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Abstract. We have studied the giant magnetoresistance of evaporated $Co_{65}Fe_{35}$/Ag alloys and we have correlated the effect with magnetization. We have observed a maximum effect of 92% at 4.2 K under a field of 60 kOe. The room-temperature effect can be roughly evaluated to 35%. The absolute decrease $\rho(0) - \rho(H)$ in resistivity plotted versus the square of magnetization shows clearly two regimes: under low fields, it presents a linear variation independent of the temperature; under high fields ($M/M_s > 0.7$), it deviates from it with an increasing slope. This behaviour is discussed in the framework of a recent model developed for granular materials.

1. Introduction

The observation of a giant magnetoresistance (GMR) effect in granular alloys [1,2] has extended a field of research concerning previously multilayered materials. These alloys are prepared by sputtering or coevaporation of immiscible magnetic and non-magnetic metals. Until now, among the different studied systems Co/Cu, Co/Ag and Fe/Ag, a Co_{28}/Ag_{72} alloy prepared by sputtering presents a maximum effect with $\Delta\rho/\rho(H) = 75\%$ at 5 K for $H = 50$ kOe [3].

A recent study [4] has correlated the GMR effect with the Curie temperature of magnetic materials, and with the atom radius ratio of the magnetic to non-magnetic metals. This last feature can be related to the discrepancy between the surface energies of the two elements which favours granule formation [5].

For two given materials, the GMR effect is now known to be dependent on the concentration of the magnetic metal and on the preparation conditions. This is caused by a dependence on the concentration of the granules and on their size. By analogy with the multilayers, this is generally interpreted with the usual two-current $\rho\uparrow$ and $\rho\downarrow$ model in terms of spin-dependent scattering of the electrons essentially at the surface of the granules and to a lesser extent within the magnetic granules. In zero field, when the orientations of the granules are random, $\rho\uparrow$ and $\rho\downarrow$ are equal, the two directions of the conduction electron spin being scattered in a similar manner by the magnetic particles. When the moments of the granules are aligned under an applied field, only one direction of the spin of the conduction electrons is scattered by the magnetic particles. The resistivity of the other direction is then substantially decreased. This results in a short-circuit effect. According to this hypothesis, Zhang and Levy [6] have developed a model relating the GMR to the magnetic particle size; the GMR is expected to be linear with the square of magnetization for a unique size, and to deviate from it under high fields for a size distribution.

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We report here a GMR study of a $Co_{65}Fe_{35}$/Ag alloy in the field range from −60 to +60 kOe and in the temperature range 4.2–244 K. The samples have been characterized by transmission electron microscopy (TEM) and magnetization measurements. The latter provides a size evaluation of the particles. We have checked the correlation between magnetization and magnetoresistance(MR) for several temperatures.

2. Sample preparation

The samples were prepared by coevaporation of $Co_{65}Fe_{35}$ (purity, 99.9%) and Ag (99.99%) on several substrates (Corning 7059 glass, Kapton and amorphous silicon) using an electron beam gun for the $Co_{65}Fe_{35}$ alloy and a Joule heating crucible for Ag. During the evaporation, the pressure was 10^{-8} Torr. The angle between the source–substrate directions and the normal to the substrate varies from 10° to 20° depending on the position of the substrate. The deposited thickness of the two elements was monitored with two quartz oscillating sensors. The deposition rate of $Co_{65}Fe_{35}$ was kept constant (0.3 Å s^{-1}) and the Ag rate was varied according to the concentration of the samples. The compositions of several samples were checked with a wavelength-dispersive x-ray spectrometer installed on a scanning electron microscope and a Castaing probe. The Fe concentration of the Fe–Co alloy in the sample is slightly higher than that of the remaining source after evaporation (for instance 38 at.% compared with 33 at.%), indicating a slightly higher Fe evaporation rate.

3. Electron diffraction and transmission electron microscopy

Special samples with a thickness of 300 Å were prepared on carbon grids for electron diffraction and TEM. The substrate temperature T_s was varied between −180 and 200 °C for a constant concentration $(Co_{65}Fe_{35})_{25}Ag_{75}$. For each sample, the use of a mask allowed the simultaneous deposition of pure Ag and Fe–Co on each side of the deposited Co–Fe/Ag alloy.

By calibrating with the pure Ag FCC diffraction pattern, we recover for the deposited $Co_{65}Fe_{35}$ alloy the BCC structure with the parameter ($a = 2.84 \pm 0.01$ Å) of the bulk material [7] (figure 1). This structure is not observed in the diffraction pattern of the (Co–Fe)–Ag alloy whatever the substrate temperature, as illustrated in figure 1 for $T_s = -180$ °C. We only observe the Ag FCC structure with a slightly reduced parameter ($a \simeq 3.97 \pm 0.01$ Å) for $T_s = -180$ °C compared with the bulk parameter ($a = 4.09$ Å), and with an identical parameter for $T_s = 100$ °C. This is in agreement with previous studies made on Co/Ag or Co/Cu alloys [8–11]; the parameter for pure Ag is recovered for high substrate temperatures as the size of the crystallites increases. Small 'poorly crystallized' particles (size, about 15 Å) of $Co_{25}Ag_{75}$ in very thin films have been observed by high-resolution TEM [12]. This can explain their absence in diffraction patterns; the observed decrease in the Ag parameter is therefore attributed to boundary strains between Ag and Co crystallites. A distinct Co FCC structure has been clearly observed for an epitaxial Co/Ag alloy [13], and for high-temperature annealed or deposited samples when the grain sizes are sufficiently large [3, 9, 11].

Using the dark-field technique, we observe, for the alloy, essentially Ag crystallites whose size is of the order of 50 Å. A clear evolution of the Ag crystallite size with the substrate temperature T_s is not observed for the present preparation conditions.

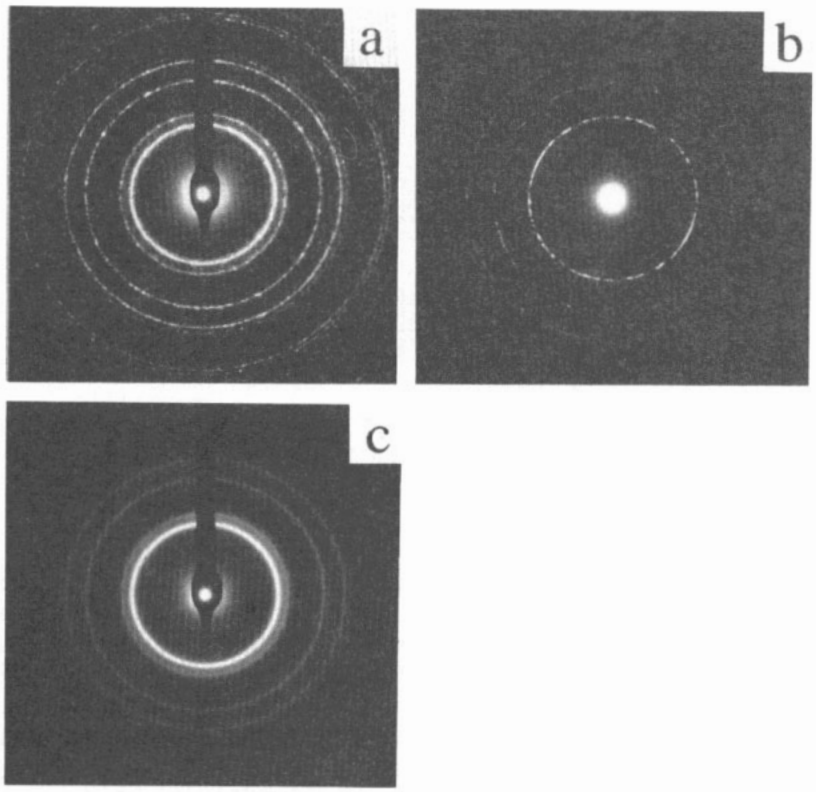

Figure 1. Electron diffraction patterns obtained for a sample deposited at −180 °C: (a) pure Ag; (b) pure $Co_{65}Fe_{35}$ alloy; (c) $(Co_{65}Fe_{35})_{25}Ag_{75}$ granular alloy.

4. Magnetization measurements

The magnetization measurements were performed with a SQUID magnetometer on samples prepared on glass or Kapton substrate. In the first case, the diamagnetic contribution arising from the glass has been linearly fitted in the field range 35–60 kOe and subtracted. In the second case, the Kapton was pasted on glass for the deposition and the magnetoresistance measurements. It was removed from the glass for magnetization measurements. With such a procedure, the diamagnetic and the low-temperature paramagnetic contributions arising from the glass substrate are avoided.

The following results have been obtained for samples 1500 Å thick deposited on Kapton at 100 °C.

The temperature dependence of the low-field ($H = 20$ Oe) magnetization after zero-field cooling, shown in figure 2 for three samples, exhibits a peak for a so-called 'blocking temperature'. This is characteristic of thermally activated dynamics above an energy barrier E_B. For particular materials, the energy barrier between easy-magnetization axes has several physical origins: magnetocrystalline, shape of the particle, and interface strains [14]. Its magnitude is proportional to the volume of the particle and to the density of anisotropy energy. On the assumption that this density is the same for all samples, the increase in the blocking temperature with increasing concentration of the magnetic alloy indicates an increase in the particle volume.

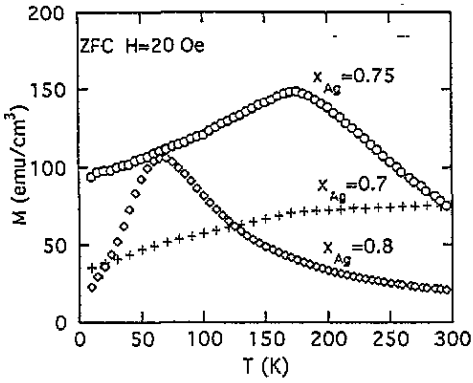

Figure 2. Temperature dependence of the magnetization of three samples $(Co–Fe)_{1-x}Ag_x$ (Kapton substrate; $T_s = 100\,°C$) measured under a field of 20 Oe after zero-field cooling.

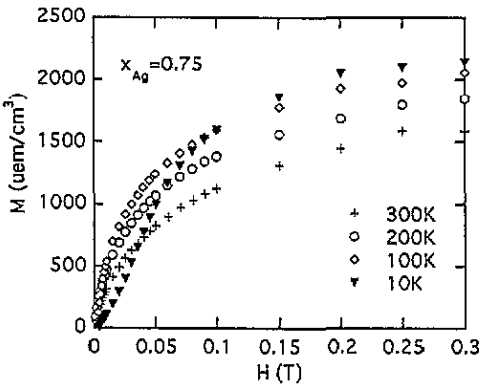

Figure 3. Field dependence of the first magnetization measured for a $(Co_{65}Fe_{35})_{25}Ag_{75}$ alloy.

The first magnetization curve, measured for several temperatures, plotted in figure 3, is also typical of 'superparamagnetic' particles for $T > T_B$. For $T < T_B$, after zero-field cooling, the system is out of equilibrium in low fields; the decrease in the measured initial susceptibility is directly due to the blocking of the particles shown above.

For a system without intrinsic anisotropy (e.g. a ferrofluid) the magnetization is given by the Langevin function. This function can also be used for a system with intrinsic anisotropy when its anisotropy energy is negligible with respect to the energy of the particle in the applied field $H(M_sVH\cos\theta$, where M_s is the saturation magnetization, V the volume of the particle and θ the angle between the particle moment and the field). In this case, one can use the high-field approximation of the Langevin function to evaluate the average volume $\langle V\rangle$ of the particle: $\langle M\rangle \simeq M_s(1 - kT/M_sH\langle V\rangle)$. In the other case (low fields), far above the blocking temperature, for uniaxial anisotropy with random direction or cubic anisotropy, the average magnetization is given by $\langle M\rangle \simeq M_s^2H\langle V\rangle/3kT$ [15].

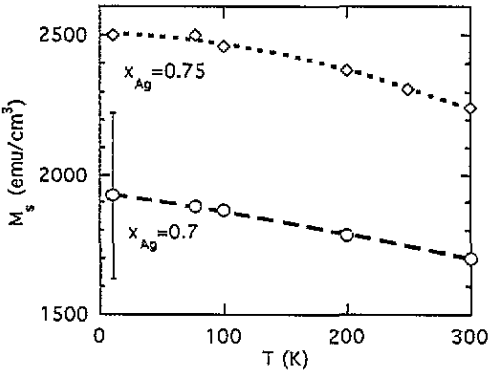

Figure 4. Temperature dependence of the saturation magnetization M_s of $(Co–Fe)_{1-x}Ag_x$ granular alloys reported in electromagnetic units per cubic centimetre of $Co_{65}Fe_{35}$ alloy.

Table 1. Size of the granules evaluated from the magnetization measurements for $(Co–Fe)_{1-x}Ag_x$ alloys. ρ_v is the volume fraction of the granules. R(LF) and R(HF) are the radii of the particles evaluated from the low- and high-field approximations, respectively, of the average magnetization. $\langle R \rangle$ is the average value of R(LF) and R(HF).

x_{Ag}	ρ_v	R(LF) (Å)	R(HF) (Å)	$\langle R \rangle$ (Å)	$\rho_v/\langle R \rangle$ ($Å^{-1}$)
0.7	0.225	—	34 ± 7	34	6.6×10^{-3}
0.75	0.184	19 ± 4	29 ± 5	24	7.6×10^{-3}
0.8	0.145	20 ± 3	22 ± 5	21	6.9×10^{-3}

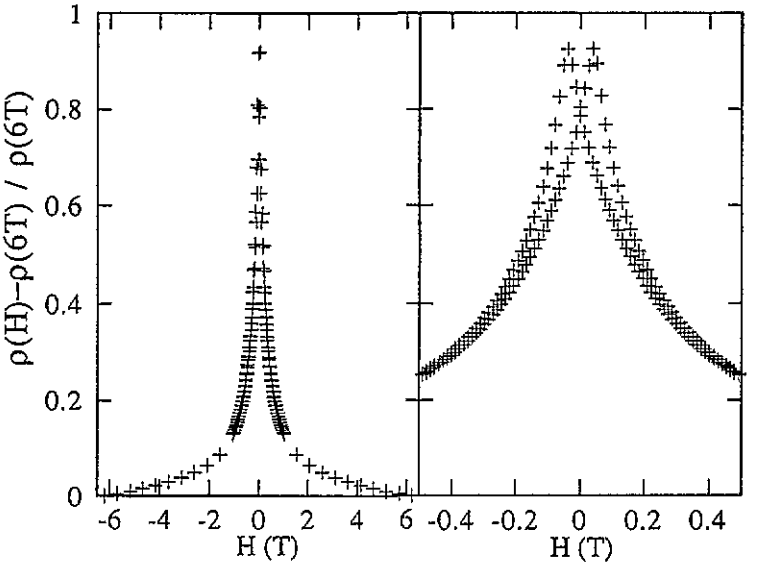

Figure 5. Example of the evolution of the MR as a function of the applied field measured at 4.2 K for an $(Co_{65}Fe_{35})_{25}Ag_{75}$ alloy 1500 Å thick deposited at 100 °C on an amorphous silicon substrate.

The determined saturation magnetization and average size of the granules are reported in figure 4 and table 1, respectively. The saturation magnetization is of the order of the value of the bulk material (1700 cmu cm^{-3} [7]). For a relatively weak field of 10 kOe, the magnetization reaches roughly 90% of its saturation value. This indicates that the Co–Fe moments are involved in particles and are not dispersed in the Ag matrix. The decrease in M_s with increasing temperature (figure 4), which is faster than that of the bulk magnetization, is often observed for small particles [16]. This effect is usually attributed to an increase in surface spin disorder (or canting) with temperature. The evaluated volume of the particle (table 1) is of the order of 25 Å. It increases with increasing Co–Fe concentration as previously reported for Co/Ag samples [5].

5. Magnetoresistance measurements

The MR has been measured with a four-point probe method in the field range from −60 to +60 kOe. A measurement current of 1 mA was used (in the ohmic regime). An example

of the MR response $(\Delta\rho/\rho)(H) = [\rho(H) - \rho(H = 60\ \text{kOe}]/\rho(H = 60\ \text{kOe})$ versus field is plotted in figure 5. We remark that it is not saturated for 60 kOe. From such curves, we deduce the parameters $\Delta\rho/\rho$ which is the MR maximum value and ΔH which is the half-width at half-maximum of the $(\Delta\rho/\rho)(H)$ peak.

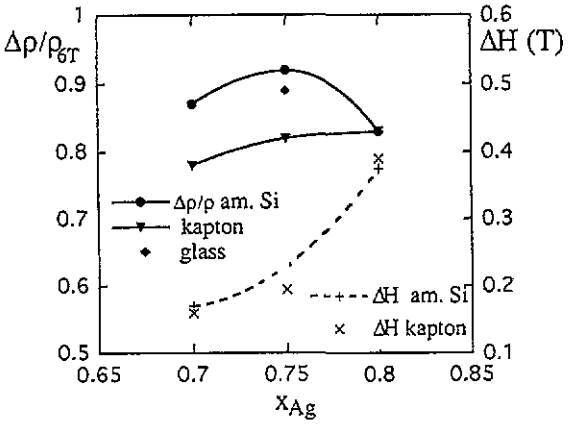

Figure 6. Maximum MR $\Delta\rho/\rho$ and half-width ΔH of the MR peak measured at 4.2 K as a function of the Ag concentration x_{Ag} of $(Co_{65}Fe_{35})_{1-x}Ag_x$ alloy for samples 1500 Å thick deposited at 100 °C on several substrates (amorphous silicon, Kapton and glass).

The MR has been measured for samples deposited on several substrates: Corning glass, Kapton and amorphous silicon (100 Å thick layer deposited on Kapton). It is plotted in figure 6 in the Ag concentration range $0.7 < x_{Ag} < 0.8$ for samples 1500 Å thick deposited at 100 °C which are the optimum thickness and substrate temperature for the MR effect [17].

The largest effect is obtained for $x_{Ag} = 0.75$ and for an amorphous silicon substrate. This optimum concentration is close to previously reported results concerning Co/Ag [4, 9, 10] or Fe/Ag [18]; it is higher than for similar sputtered samples [19]. $\Delta\rho/\rho$ slightly varies in the measured concentration range although the number of magnetic atoms has been varied by a factor of 1.5. This effect can be related to the decrease in the particle volume fraction ρ_v and radius R with increasing x_{Ag}. In a primary approximation, the magnetic contribution to the resistivity is expected to increase with increasing product cS (where $c = \rho_v/V$ is the concentration of the granules, V the volume of the granules and S their surface) owing to spin-dependent interfacial scattering (we neglect scattering inside the particles). cS is proportional to ρ_v/R. The estimated ratio ρ_v/R reported in table 1 varies slightly with x_{Ag} in a similar way as $\Delta\rho/\rho$.

We observe an increase in the linewidth ΔH with increasing x_{Ag}. As the size of the granules decreases with increasing x_{Ag}, the behaviour of ΔH can be easily attributed to poor alignment of smaller particles by the applied field (the alignment being governed by the ratio $M_s V H/kT$).

6. Temperature and field dependences of the magnetoresistance

We have studied the evolution of $\Delta\rho(H)/\rho(H) = [\rho(H = 0) - \rho(H)]/\rho(H)$ with the measuring temperature for a sample which presents one of the maximum MR effect

($x_{Co-Fe} = 0.25$; $T_s = 100\,°C$; $e = 1500$ Å; deposited on glass). This evolution is plotted in figure 7 for two fields: 10 and 60 kOe. $\Delta\rho(H)/\rho(H)$ continuously decreases as the temperature increases similarly to previous results observed for samples with a large MR effect [2, 3, 9]. Two features influence this behaviour: the increase in resistivity $\rho(H)$ versus temperature and the decrease in $\Delta\rho$ [3] as shown in figure 7. The temperature dependence of $\Delta\rho$ is mainly due to a decrease in the average magnetization with increasing temperature. By extrapolating to room temperature, we can evaluate a MR effect of about 20% for $H = 10$ kOe comparable with Co/Ag evaporated alloy [4, 5].

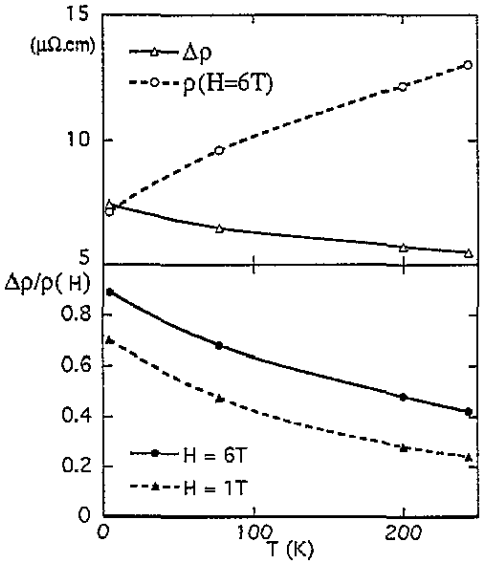

Figure 7. Temperature dependence of the MR $\Delta\rho/\rho(H) = [\rho(0) - \rho(H)]/\rho(H)$ for $H = 10$ and 60 kOe, of $\Delta\rho = \rho(0) - \rho(H = 60$ kOe) and of $\rho(H = 60$ kOe) for a $(Co_{65}Fe_{35})_{25}Ag_{75}$ alloy 1500 Å thick deposited at 100 °C on a glass substrate.

We have plotted in figure 8 the absolute resistivity decrease $\Delta\rho = \rho(H = 0) - \rho(H)$ as a function of $M^2(H)$ for several temperatures. We can clearly distinguish two regimes in the variation in $\Delta\rho$ with M^2: for instance, at $T = 77$ K, when $M/M_s \leqslant 0.7$, $\Delta\rho$ varies linearly with M^2 with a slope which appears to be temperature independent; when $M/M_s \geqslant 0.7$, it presents a deviation from this linear behaviour which increases with increasing temperature.

Let us first consider the low-field regime ($M/M_s \leqslant 0.7$). Our observation is in agreement with the model of Zhang and Levy [6] which was developed for granular systems. In this model, a linear dependence of $\Delta\rho$ on M^2 is obtained for a unique size of particles in the entire field range and also for a size distribution in the low-field regime ($M/M_s \leqslant 0.7$). The fact that the same behaviour is observed for several temperatures shows that $\Delta\rho$ and M^2 are the relevant parameters, $\Delta\rho$ being a function of only the average magnetization. $\Delta\rho/\rho$ plotted as a function of $(M/M_s)^2$ would exhibit a temperature-dependent slope due only to the variation in ρ and M_s with the temperature. $\Delta\rho$ seems to be insensitive, in this field regime, to the increasing disorder of the surface spin with temperature, whose influence was previously expected [20]. This result is reminiscent of the observation made on a multilayered system where the linear variation in $\Delta\rho$ with M^2 is temperature independent [21].

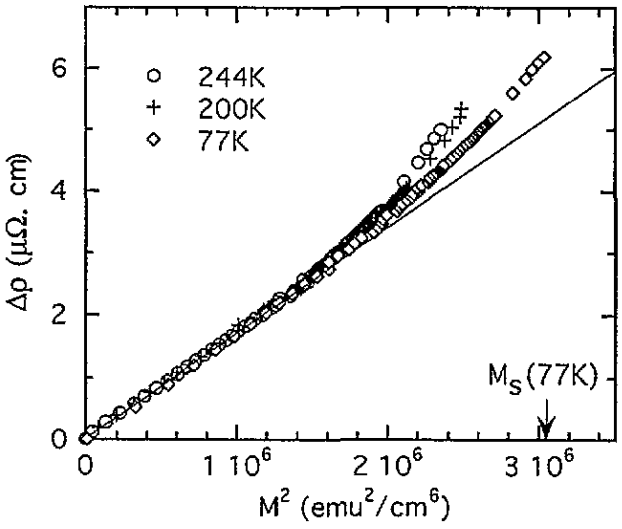

Figure 8. Absolute resistivity decrease $\Delta\rho = \rho(0) - \rho(H)$ as a function of the square M^2 of the magnetization (reported in square electromagnetic units per (centimetre)^6 of Co–Fe alloy) for a $(Co_{65}Fe_{35})_{25}Ag_{75}$ granular alloy 1500 Å thick deposited at 100 °C on a glass substrate.

We focus now on the high-field regime which appears more specific to a granular system. A deviation in $\Delta\rho$ from a M^2 law has already been noted in a previous study [1]. On the contrary, a linear dependence of $\Delta\rho$ on M^2 for $0 \leqslant M/M_s \leqslant 1$ has been observed with samples for which the size of the granules is supposed to be more homogeneous [22].

A deviation in $\Delta\rho(M^2)$ from its linear slope is predicted by Zhang and Levy when considering a volume distribution $f(V) \propto 1/V$ with $0 \leqslant V \leqslant V_{max}$. The deviation is then directly due to the contribution of the very small particles. Although we do not exclude a contribution from a size distribution, such a particular distribution (with an increasing number of particles with decreasing size) has never been observed in granular alloys and seems quite unrealistic; we expect the actual distribution to be rather a Gaussian or a log-normal type with a minimum ferromagnetic domain size.

Another contribution to the increasing slope of $\Delta\rho$ with increasing M^2 could be given by the alignment of the disordered surface spin under a very high field. This effect has been observed for iron particles in an insulating matrix [16]. In our case, it could increase the spin-dependent scattering potential of the interfaces and could then have a non-negligible effect on $\Delta\rho$.

The surface spin disorder which increases with increasing temperature could also influence the temperature dependence of $\Delta\rho$. It is the main cause of the decrease in the resulting magnetic moment of the particle with increasing temperature (the other cause being the decrease in the magnetization of the core of the particle due to spin waves). This decrease can be interpreted by a decrease in M_s (keeping V constant) as has been reported above or by a decrease in V (keeping M_s constant). Considering the second case, the increase in the particle surface spin disorder would shift the size distribution towards small volumes when the temperature is increased. According to model of Zhang and Levy (where the small particles have a greater relative contribution to the MR than to the magnetization) this shift would induce a larger deviation of $\Delta\rho$ from the linear behaviour at high temperatures, in agreement with our observations.

7. Conclusion

We have observed a maximum MR effect of 92% at 4.2 K ($H = 60$ kOe) for a $Co_{65}Fe_{35}$/Ag alloy 1500 Å thick evaporated on an amorphous silicon substrate at 100 °C. Sample characterization has been made using magnetization measurements and electron diffraction. The absolute resistance difference $\rho(H = 0) - \rho(H)$, reported as a function of the square of the magnetization M^2, exhibits two regimes. Firstly, it varies linearly with M^2 in low fields $M/M_s \leqslant 0.7$. In the high-field regime, $\rho(H = 0) - \rho(H)$ deviates from the linear behaviour with an increasing slope. This seems to be specific for granular systems and could be related to a size distribution effect or to the disorder of the granules surface spins.

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