Controlling exchange bias in Co–CoO$_x$ nanoparticles by oxygen content

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Received 30 July 2008, in final form 25 February 2009
Published 3 April 2009
Online at stacks.iop.org/Nano/20/175702

Abstract
We report on the occurrence of exchange bias on laser-ablated granular thin films composed of Co nanoparticles embedded in an amorphous zirconia matrix. The deposition method allows one to control the degree of oxidation of the Co particles by tuning the oxygen pressure at the vacuum chamber (from $2 \times 10^{-5}$ to $10^{-1}$ mbar). The nature of the nanoparticles embedded in the nonmagnetic matrix is monitored from metallic, ferromagnetic (FM) Co to antiferromagnetic (AFM) CoO$_x$, with a FM/AFM intermediate regime for which the percentage of the AFM phase can be increased at the expense of the FM phase, leading to the occurrence of exchange bias in particles of about 2 nm in size. For an oxygen pressure of about $10^{-3}$ mbar the ratio between the FM and AFM phases is optimum with an exchange bias field of about 900 Oe at 1.8 K. The mutual exchange coupling between the AFM and FM is also at the origin of the induced exchange anisotropy on the FM leading to high irreversible hysteresis loops, and the blocking of the AFM clusters due to proximity to the FM phase.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Magnetic nanoparticles [1] have attracted great interest during the last decades due to their technological applications in magnetic recording [2], magnetic resonance imaging [3, 4], non-linear optics [5] and various biomedical applications [6]. As a result of their reduced dimensions, nanoparticles display magnetic and transport properties that differ from their bulk counterparts [1], as a consequence of the interplay among finite size and surface effects, and interparticle interactions. Besides, particle surfaces may be easily oxidized resulting in core–shell structures, which can also be produced by physical and chemical procedures [7, 8]. Of particular interest is the case when a ferromagnetic (FM) core is surrounded by an antiferromagnetic (AFM) shell, leading to the appearance of the so-called exchange bias (EB) phenomenon [9, 10]. EB is a proximity effect [11] arising from the exchange coupling at the interface between a FM and an AFM which are in intimate contact. EB is usually described as an additional unidirectional anisotropy induced by the AFM material into the FM one, which yields a shift in the magnetic hysteresis loop along the magnetic field axis, below the AFM ordering temperature. The magnitude of this shift is defined as the EB field, $H_{cb}$. Although EB was first observed in partially oxidized Co particles with a FM/AFM core/shell structure [9, 12] most studies have focused on layered AFM/FM systems [13] due to their applications in advanced magnetic devices, such as read heads in magnetic recording and magnetic random access memories. Loop shifts as a function of the FM/AFM thickness ratio [10], coercive field enhancement [10], double hysteresis loops [11, 14, 15] and unusual magnetization reversal [16–18] are among the most investigated EB effects.

Nowadays, EB continues to attract a lot of interest from the fundamental and technological points of view, not only due to its potential applicability but also because there is still a lack of microscopic understanding of the phenomenon (for recent reviews see [10, 16, 19]). Moreover, it has been shown that control of the exchange interactions between the FM particle surface and an AFM embedding matrix can be a means to beat the superparamagnetic limit [20, 21]. It is worth
noting that at the interface of core/shell nanoparticles there exist roughness and non-compensation of the magnetization which are two of the main ingredients in the models for EB in thin films [22, 23]. Some of us recently showed that $H_{ab}$ in FM/AFM core/shell nanoparticles can be accounted for by a microscopic model taking into account the exchange interactions and net magnetization due to uncompensated spins both at the AFM/FM interface [24].

Some of the largest $H_{ab}$ have been reported for partially oxidized nanoparticles with a FM/AFM core/shell structure, Co/CoO$_x$ deserving special attention (loop shifts up to 10.2 kOe after field cooling the sample under 50 kOe have been reported for particles of 6 nm in size [25]; for a complete set of references see [16, 19]). EB has also been studied in several nanoparticulate systems obtained by different physical fabrication techniques, e.g. gas phase condensation method [26], ball milling and hydrogen reduction [27], sputtering [28, 29], solid state reaction method [30], dual laser evaporation source [14] and pulsed laser ablation [31].

In this work, we report on the occurrence of EB in granular films composed of Co nanoparticles embedded in a Y-stabilized amorphous zirconia matrix, which have been deposited by laser ablation. This method allows one to control the degree of oxidation of the Co particles just by tuning the oxygen pressure at the vacuum chamber during deposition, without any subsequent annealing. Consequently, we monitor the nature of the nanoparticles embedded in the nonmagnetic matrix from pure FM to pure AFM, with a FM/AFM intermediate regime for which the percentage of the AFM phase may be increased at the expense of the FM phase.

2. Experimental details

Granular films composed of Co nanoparticles embedded in an amorphous zirconia (ZrO$_2$) matrix were obtained by pulsed laser ablation [32–35] in the presence of an oxygen partial pressure. Zirconia was stabilized with 7 mol% Y$_2$O$_3$ which provides the matrix with good oxidation resistance, a thermal expansion coefficient matching that of metal alloys and very high fracture toughness values. Zirconia perfectly coats metallic nanoparticles and enables the occurrence of very sharp particle–matrix interfaces [32–36]. We used a KrF laser with wavelength of 248 nm, pulse duration of 34 ns and a composite rotary target to deposit simultaneously cobalt and zirconia. The pulse frequency (10 Hz), fluence (2 J cm$^{-2}$) and the laser spot (3 mm$^2$) were fixed for all samples, as well as the deposition temperature (295 K) and base pressure at the vacuum chamber (lower than 10$^{-4}$ mbar). The Co/zirconia ratio in the composite target was also fixed for all samples and was chosen to grow granular films below the percolation threshold. We note that the sample grown at the base pressure had a volume Co fraction, $x_v$, of about 0.23. The degree of oxidation of the Co nanoparticles was controlled by varying the O$_2$ pressure in the chamber from $2 \times 10^{-5}$ (oxygen base pressure) to 0.1 mbar. It was assumed that the oxidation of the nanoparticles takes place essentially during their flight from the target to the substrate surface. Six samples were synthesized for the magnetic study at the following values of O$_2$ pressure: $2 \times 10^{-5}$, $2.5 \times 10^{-4}$, $0.7 \times 10^{-3}$, $10^{-3}$, $10^{-2}$ and 10$^{-1}$ mbar.

Average sample composition was determined by microprobe analyses. The films were structurally characterized by high resolution transmission electron microscopy (HRTEM) which was carried out on samples deposited onto a silicon nitride membrane window, allowing direct observation of as-deposited samples. The particle size distributions were also obtained by fitting the high temperature isothermal magnetization curves to a distribution of Langevin functions which model the superparamagnetic behaviour of the samples.

The degree of oxidation of the Co particles as a function of the oxygen partial pressure was analysed by x-ray photoelectron spectroscopy (XPS). The XPS spectra for the O 1s, Co 2p$_{3/2}$ and 2p$_{1/2}$, Zr 3d$_{5/2}$ and 3d$_{3/2}$, Y 3d$_{5/2}$ and 3d$_{3/2}$ and C 1s core levels were recorded using the Al K$_\alpha$ emission line ($h\nu = 1486.6$ eV; incident angle of the beam $= 45^\circ$). Spectra were obtained before and after 10 min of an in situ low-energy (4 keV) sputtering process (incident at 45°) to avoid the contribution from the oxidized particles at the free surface of the thin films. Energy calibration was carried out by adopting the C 1s core level, associated with the usual surface contamination layer (binding energy $E_B = 284.8$ eV), as a reference peak [37].

Magnetization measurements were carried out in a SQUID magnetometer. The temperature dependence of the magnetization under 50 Oe after field cooling (FC) and zero field cooling (ZFC) the sample, and the hysteresis loops at various temperatures up to a maximum field of 50 kOe were recorded.

3. Structural characterization

Average sample composition was determined by electron microprobe analyses, being $x_v$ (the Co volume fraction) below 0.23 and decreasing with increasing oxygen pressure. For all the studied samples the Co content was well below the percolation threshold $x_v \approx 0.35$ [34].

Figure 1 shows HRTEM images corresponding to a sample with metallic Co nanoparticles, obtained at the base oxygen pressure in the vacuum chamber, and another one grown at $P_{O_2} = 5 \times 10^{-4}$ mbar. As an example of the first case, figure 1(a) shows a bright field HRTEM of a nanoparticle where the dark regions correspond to Co and the light ones to the amorphous ZrO$_2$ matrix. The microstructure is very clean: the lattice fringes indicate single crystalline Co particles and the particle–matrix interfaces are sharp, as observed in many other granular systems prepared by pulse laser deposition [34, 35]. Selected area electron diffraction patterns can be fitted to metallic fcc Co. Figure 1(c) shows the particle size distribution obtained from HRTEM images corresponding to the sample prepared at the oxygen base pressure. The average particle diameter is about 2.7 nm with a standard deviation of 0.7 nm, which indicates a narrow size distribution. For the second case (see figure 1(c) for the sample grown at $P_{O_2} = 5 \times 10^{-4}$ mbar), several lattice fringes, oriented in different directions, can be observed within one particle together with an amorphous irregular halo surrounding
Figure 1. HRTEM images for the samples deposited at $P_{O_2}$: (a) $2 \times 10^{-5}$ and (c) $5 \times 10^{-4}$ mbar. White lines in (c) circle Co regions while black line circles CoO ones. The size distribution determined from HRTEM images corresponding to the sample deposited at a base pressure of $2 \times 10^{-5}$ mbar is shown in panel (b). Panel (d) shows the Fourier transform of the image in (c), where the obtained diffraction pattern was indexed to both fcc Co and CoO reflections.

The particle without any clear interface. Figure 1(d) shows the Fourier transform of the image in figure 1(c), where the diffraction pattern can be indexed to both Co and CoO reflections. The crystallographic interplanar distances, determined from the diffraction pattern in figure 1(d), are $0.200 \pm 0.007$ nm for Co(111) (expected value $0.2046$ nm), $0.25 \pm 0.01$ nm for CoO(111) (expected value for CoO $0.2455$ nm) and $0.22 \pm 0.01$ nm for CoO(200) (expected value for CoO $0.2126$ nm), in good agreement with the expected values for both metallic and oxidized cobalt. Therefore, within these polycrystalline nanoparticles some areas correspond to Co regions while others correspond to CoO$_x$. Besides, particles seem to be larger in the oxidized sample, probably due to the fact that the presence of O$_3$ at the vacuum chamber during the deposition impedes the small particles arriving on the substrate and results, together with the cell expansion due to oxidation, in the shift of the particle size distribution to higher values. Amorphous CoO$_x$ may be very difficult to distinguish from the zirconia matrix, so CoO$_x$ clusters are probably only observed when they are aggregated with metallic Co particles. We note that the zirconia matrix starts to crystallize when the sample is overexposed under a high-electron current.

Further information about the degree of oxidation of the Co particles as a function of oxygen partial pressure can be gained by analysing XPS data. Figure 2 shows the Co 2p$_{3/2}$ and 2p$_{1/2}$ core levels for three values of the oxygen partial pressure, both before and after sputtering the surface. As expected, the only peaks observable before sputtering correspond to Co–O bonds (at about $780.0$–$780.7$ eV and $795.4$–$796.2$ for the 2p$_{3/2}$ and 2p$_{1/2}$ contributions, respectively, in figure 2), while there is no trace of Co–Co bonds characteristic of metallic Co which should appear at $778.1$–$778.3$ eV (2p$_{3/2}$) and $793.1$–$793.3$ eV (2p$_{1/2}$). For a general reference on binding energies see, for example, [38]. In contrast, once the oxidized surface layer is removed by sputtering, the degree of oxidation of the remaining Co nanoparticles increases with increasing oxygen partial pressure in the chamber during deposition. For the sake of simplicity just three examples are shown as being representative of the overall behaviour. For the lowest oxygen pressure ($P_{O_2} = 2 \times 10^{-5}$ mbar) only the peaks corresponding to metallic Co–Co bonds are observed (see figure 2(a)), in agreement with the HRTEM image in figure 1(a). In the case for $P_{O_2} = 10^{-3}$ mbar (figure 2(b)) the peaks corresponding to both Co–Co and Co–O bonds are observed, indicating that the particles are partially oxidized, in agreement with the HRTEM image in figure 1(c). At about the highest oxygen pressure in this work ($P_{O_2} = 0.1$ mbar, figure 2(c)) Co nanoparticles are almost completely oxidized since the peaks corresponding to the Co–O bonds are the unique contribution to the 2p core level. The XPS data confirm that Co clusters get oxidized during their flight from the target to the substrate due to reaction with the remaining oxygen in the deposition chamber. The difference in the peak intensity between pre-sputtering and post-sputtering spectra in figure 2 arises from the distinct time of exposure (longer for the case of post-sputtering spectra). The peaks corresponding to Zr 3d$_{5/2}$ and 3d$_{3/2}$ core levels, which are observable before and after sputtering the surface of the samples, are associated with Zr–O bonds (at about the
expected 182–182.5 eV and 184–184.5 eV for the 3d_{3/2} and 3d_{5/2} contributions, respectively [38]), without any indication of the existence of metallic Zr–Zr bonds. Besides, XPS spectra for Zr core levels do not show any significant dependence on the partial oxygen pressure in the chamber. As far as Co is concerned, the Co/CoO atomic fraction is about 0.9 ± 0.1 for the sample grown at \( P_{O_2} = 10^{-3} \) mbar (figure 2(b)).

4. Magnetic characterization

Figure 3 shows the ZFC and FC curves of samples obtained at different \( P_{O_2} \). Figure 3(a) shows the case corresponding to metallic FM Co nanoparticles embedded in the zirconia matrix (ablated at the base pressure) which exhibits all the features that are characteristic of a narrow distribution of slightly interacting small FM particles. As \( P_{O_2} \) increases, a variety of effects can be observed: (i) the magnetization of the samples decreases due to the decrease in the FM fraction, at the expense of the increase in the AFM CoO\(_x\) phase (see below); (ii) the position of the ZFC peak shifts and broadens from 6.5 K for \( P_{O_2} = 2 \times 10^{-5} \) mbar to 12.5 K for \( P_{O_2} = 10^{-3} \) mbar, suggesting the occurrence of exchange coupling between the AFM and FM phases [20, 21], and/or the shift to higher values of the particle size distribution; (iii) the increase in the temperature of the onset of the ZFC–FC irreversibility suggests the existence of interacting FM clusters inside partially oxidized aggregates, also supported by HRTEM images, which broaden the distribution of particle relaxation times; and (iv) the increase in the FM background at high temperatures which indicates the presence of some large FM aggregates.

One might expect that in the superparamagnetic regime magnetization curves should scale when plotted as a function of \( H/T \). Figure 4 shows such plot for four representative cases with increasing \( P_{O_2} \) and, hence, AFM/FM ratio for several temperatures. The magnetization curves for metallic FM Co nanoparticles scale perfectly (figure 4(a)), while the quality of this scaling gets gradually worse as \( P_{O_2} \) increases (see figures 4(b) and (c)). The scaled curves for the sample ablated at the base pressure can be well fitted to a log-normal distribution of Langevin functions (solid line in figure 4(a)), leading to a mean particle size of 1.8 nm and standard deviation of 0.2 nm, in agreement with the ZFC curve in figure 3(a) and the size distribution in figure 1(b), suggesting a very narrow distribution of FM particles. In this fit, it was assumed that all particles have the Co bulk saturation magnetization of 0.15 \( \mu_B \) Å\(^{-3} \). Therefore, the slight discrepancy between the obtained values of the average crystalline and magnetic sizes could arise from a reduced value of the particle magnetization due to surface disorder and finite size effects. The effect of the progressive oxidation of the FM particles with increasing oxygen pressure may be well understood in figure 4(c) where magnetization curves result from the superimposition of two contributions: the magnetization of the FM components through Langevin terms and an AFM component which yields a linear term on the magnetic field. While the Langevin terms scale on \( H/T \), this is not the case of the AFM components as reported in [39]. This is the main reason for the lack of scaling in figures 4(b) and (c). Assuming that the AFM components arise from superparamagnetic CoO\(_x\) clusters, the magnetization curves in figures 4(b) and (c) at 300 K, which is close to the Néel temperature of bulk CoO, can be fitted to a distribution of Langevin functions without a linear AFM term, yielding a mean particle size of 2.7 nm with a standard deviation of 0.3 nm and 3.4 nm with a standard deviation of 0.4 nm. The increases in the mean particle size and standard deviation are in agreement with the shift and broadening of the ZFC curves in figure 3. It is worth noting that the ZFC curves measured at low fields are mostly due to the FM contribution while both AFM and FM components contribute to the magnetization curves as a function of \( H \). Interestingly enough, figure 4(d) shows magnetization curves for a case with completely oxidized Co particles \( (P_{O_2} = 0.1 \text{ mbar}) \) within the low temperature range 2.7–20 K. As the FM component has disappeared completely, the \( H/T \) scaling resembles that of a distribution of superparamagnetic AFM particles with uncompensated spins [39]. The magnetization curves can be fitted to a distribution of Langevin functions yielding a mean value of the uncompensated spins per cluster below about 5\( \mu_B \), suggesting that the AFM clusters are very small.

The drastic modification of the magnetic properties of the granular films depending on the AFM/FM ratio can be further investigated in figure 5 where the hysteresis loops at...
Figure 4. Magnetization against $H/T$ for the samples prepared at $P_{O_2}$: (a) $2 \times 10^{-5}$, (b) $7 \times 10^{-4}$, (c) $10^{-3}$ and (d) 0.1 mbar. For (a)–(c), the triangles (black) correspond to 100 K, the circles (blue) to 200 K, and the squares (red) to 300 K. For (d) the triangles (black) correspond to 2.7 K, the circles (blue) to 5 K, the diamonds (green) to 10 K and the squares (red) to 20 K.

5 K after a ZFC process are depicted. Figure 5(a) shows the characteristic hysteresis loop of an assembly of blocked FM Co nanoparticles as expected for the sample deposited at the base pressure. With the increase in $P_{O_2}$ an additional AFM contribution superimposes the central FM hysteresis loop. Up to about $P_{O_2} = 10^{-3}$ mbar there still survives a significant FM fraction which is blocked at 5 K and is exchange coupled to the AFM clusters, such that the AFM regions are also blocked by proximity to the FM (see figures 5(b) and (c)). This proximity effect and the resulting induced anisotropy are at the origin of the high irreversibility in the hysteresis loops in figures 5(b) and (c). By further increasing $P_{O_2}$ the amount of the AFM component grows at the expense of the FM one, such that as the exchange coupling progressively disappears, the AFM component becomes superparamagnetic and the irreversibility in the hysteresis loops vanishes (see figures 5(d) and (e)). All of the foregoing demonstrate that it is necessary to have a minimum amount of both FM and AFM phases for exchange coupling to show up [16, 20].

5. Exchange bias

In order to gain a deeper insight into the nature of the exchange coupling phenomenon taking place between the FM and AFM phases as a function of $P_{O_2}$, hysteresis loops after field cooling the sample at 50 kOe from room temperature down to the
measuring temperature were recorded within the range 1.8–16 K. Figure 6 shows an example where a shifted loop is observed as a consequence of EB between the FM and AFM phases, showing $H_{eb} = 900$ Oe at 1.8 K. The magnetic irreversibility is evident. Note that, in this case, the maximum applied field was lower than the irreversibility field, so the observed loop shift may not entirely correspond to an EB phenomenon because the measured hysteresis loop could be a minor loop.

The EB ($H_{eb}$) and coercive field ($H_c$) as functions of $P_{O_2}$ are shown at 5 K in figure 7. Both $H_c$ and $H_{eb}$ progressively increase with the degree of oxidation of the metallic component up to about $P_{O_2} = 0.7 \times 10^{-3}$ mbar, yielding maximum values of $H_{c}^{\text{max}} = 918$ Oe and $H_{eb}^{\text{max}} = 73$ Oe at 5 K. Consequently, the optimum ratio between the FM and AFM components occurs at about this pressure. XPS data (figure 2(b)) suggest that this optimum value corresponds roughly to half of the Co atoms being oxidized. The fact that the coercive field of the FM phase also increases as the EB develops gives further support to the existence of exchange coupling. Above that optimum pressure both $H_c$ and $H_{eb}$ decrease and vanish completely at about $P_{O_2} = 0.1$ mbar as the FM phase disappears. This evolution is associated with the progressive change in the FM/AFM ratio from metallic FM Co—characterized by small $H_c$ and zero $H_{eb}$—to the pure AFM CoO$_x$ with zero $H_c$ and $H_{eb}$. For the intermediate cases the characteristic EB behaviour arising from the exchange coupling between the FM and AFM phases is observed.

The dependences of $H_c$ and $H_{eb}$ on temperature are shown in figure 8. A remarkable maximum value of $H_{eb} = 900$ Oe is observed for $P_{O_2} = 10^{-3}$ mbar at 1.8 K. The decrease of $H_c$ and $H_{eb}$ with increasing temperature follows the onset of superparamagnetism as displayed in the ZFC–FC curves. $H_{eb}$ increases gradually for all temperatures with the increase of $P_{O_2}$ during the ablation from $2.5 \times 10^{-4}$ to $10^{-3}$ mbar. $H_c$ follows a more complex trend. At 1.8 K, $H_c$ for $P_{O_2} = 10^{-3}$ mbar is less than that for $7 \times 10^{-4}$ mbar due to the magnetic frustration associated with the FM–AFM interactions as typically observed in disordered magnets. This magnetic frustration also produces a smoother $H_c(T)$ for $P_{O_2} = 10^{-3}$ mbar than those for the other two samples in figure 8, for which $H_{eb}$ is smaller, yielding a crossing among the $H_c(T)$ curves. This effect results in the stabilization of the FM phase due to the exchange coupling to the AFM phase.

6. Conclusions

The occurrence of EB has been shown in partially oxidized Co particles of about 2 nm. This size is at the lowest limit reported for the occurrence of EB in Co/CoO core/shell structures (3 nm) [40] and Co clusters embedded in a CoO matrix (2.5 nm) [41]. This critical size might be due to both the effective Zeeman energy of the FM and the anisotropy energy of the AFM. For oxygen pressure of about $10^{-3}$ mbar the ratio between the FM Co and AFM CoO$_x$ phases is optimum (about 50% each) with an EB field close to 1 kOe at 1.8 K after a FC of 50 kOe. The occurrence of this EB field may be related to the polycrystalline nature of the nanoparticles in which Co and CoO$_x$ nanocrystalline clusters coexist in intimate contact. The mutual exchange coupling between the AFM and FM phases due to proximity results not only in loop shifts but also in: (i) the blocking of small AFM clusters when
the FM phase is also blocked; (ii) the high irreversibility in the hysteresis loops due to the induced exchange anisotropy and magnetic frustration associated with AFM–FM interactions as observed in many magnetically disordered systems; and (iii) the thermal stabilization of the FM as both observed in the smooth temperature dependence of the coercive field and the increase in the temperature of the maximum of the ZFC curve.

Acknowledgments

We would like to thank the staff of the Scientific and Technical Facilities of the University of Barcelona. Financial support of the Spanish CICYT (MAT2006-03999) and Catalan DURSI (2005SGR00969) is gratefully recognized. MK thanks the Spanish MEC for financial support through a PhD grant.

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Figure 8. Temperature dependence of the EB (H_{eb}) (empty red symbols) and coercive field (H_c) (solid black symbols) for the samples prepared at P_{o2}: 2.5 \times 10^{-4} (squares), 7 \times 10^{-4} (circles) and 10^{-3} (triangles) mbar.