CoO$_{1-\delta}$ layers in a reactivity sputtered exchange-bias system

J M Riveiro$^1$, P S Normile$^{1,2,3}$, J A De Toro$^{1,3}$, T Muñoz$^1$, P Muñiz$^1$, J A González$^1$ and J P Andrés$^1$

1 Departamento de Física Aplicada, Universidad de Castilla-La Mancha, 13071 Ciudad Real, Spain
2 XMaS UK-CRG, European Synchrotron Radiation Facility, F-38043 Grenoble, France
E-mail: peter.normile@esrf.fr and JoseAngel.Toro@uclm.es

New Journal of Physics 10 (2008) 083028 (13pp)
Received 5 June 2008
Published 19 August 2008
Online at http://www.njp.org/
doi:10.1088/1367-2630/10/8/083028

Abstract. In exchange-bias (EB) systems involving CoO as the antiferromagnetic (AF) component, preparation of overoxidized (i.e. CoO$_{1+\delta}$) AF layers has previously been shown to have an important effect on EB properties, which arises due to point defects associated with the non-stoichiometric material. Here, we present a study on the effect of post-deposition annealing to progressively higher temperatures, $T_{\text{ann}}$, on magnetic and structural parameters of a [Co/CoO/Ag]$_{30}$ multilayer. Our results indicate a different AF layer stoichiometry: CoO$_{1-\delta}$ (i.e. underoxidized), with $\delta = 0.1$ for the as-deposited sample. The annealing behaviour of the different parameters is explained via a mechanism of thermally induced diffusion of Co ions from the oxide to the Co layers, which is initiated at $T_{\text{ann}} \approx 300^\circ$C ($= T^*$) and leads to the approach to stoichiometry (i.e. Co$_1$O$_1$) in the AF layers. We suggest why our sample preparation conditions could have led to this unusual (i.e. CoO$_{1-\delta}$) stoichiometry and comment on possible future studies.
Driven by its relation to future technology, as well as by the pursuit of understanding ever increasingly complex scenarios in condensed matter physics, research into the exchange-bias (EB) effect continues to thrive, more than 50 years after its discovery [1]. The magnitude of the effect—namely the size of the horizontal shift ($H_E$) in the hysteresis loop of a ferromagnetic (F)/antiferromagnetic (AF) system after the latter component has ordered in the presence of a magnetized F component [1]—is often understood to be governed by factors associated with the AF component (e.g. the atomic scale roughness [2], domain configuration [3] and in-plane grain size [4]), which control the EB effect via their relationship to interfacial uncompensated spins [5]. Recently, there has been a great deal of interest in the effect of substitutional point defects in the AF component on EB properties of F/AF bilayer systems, where the cases of defects produced via dilution by a nonmagnetic impurity element [6]–[8] and overoxidation [6, 9, 10] (i.e. CoO$_{1+\delta}$ AF) have been studied. In those works, the influence of the defects on EB has been explained using the domain state model [6], which is again related to uncompensated spins, but in the bulk of the AF layer as well as at the interface [7, 8].

In the present paper, in contrast to the previous studies involving an overoxidized AF component (CoO$_{1+\delta}$) [6, 9, 10], we present an annealing study on a F/AF multilayered system, the results of which are strongly suggestive of the possibility of AF layers that are initially slightly underoxidized (viz CoO$_{1-\delta}$ with $\delta = 0.1$). The main result is that of a strong correlation observed between the annealing dependence of $H_E$—which begins to fall monotonically at $T_{\text{ann}} \approx 300 \, ^\circ\text{C}$ ($= T^*$) in accordance with an Arrhenius law—and that of other magnetic and structural properties. Since our proposed stoichiometry implies a Co excess in the AF layers (i.e. CoO$_{1-\delta}$ is equivalent to Co$_{1+\delta}$O for small $\delta$), the present work constitutes an example of the seldom studied case of magnetic impurities in the AF component of an EB system [11].

2. Experimental details

Very recently, we demonstrated that sequential sputter deposition of Ag and Co layers in an oxygen atmosphere of a certain pressure ($p_{O_2} = 2 \times 10^{-5}$ mbar) provides a means to fabricate multilayer samples comprising magnetic layers of essentially a Co/CoO bilayer morphology sandwiched between nonmagnetic (Ag) layers [12]. To briefly summarize, our demonstration was based, principally, on two pieces of information, additional to x-ray reflectivity results. Firstly, measurements using an optical technique (GDOES) observed peak signals from cobalt...
and oxygen that were separated in (etch) time, indicating Co/CoO bilayers rather than, for example, a morphology comprising Co nanoparticles embedded in CoO layers, for which the (Co and O) signals would be expected to coincide. Secondly, the room temperature hysteresis loops had a ferromagnetic character and displayed a strong anisotropy between the in- and out-of-plane directions, whereas when Co was deposited onto discontinuous Ag layers the loops showed a superparamagnetic character, with little difference between in-plane and out-of-plane applied field directions.

In the present study, a similar Co/CoO/Ag multilayer system (with continuous Ag layers) has been investigated. Specifically, the sample comprised 30 repeat magnetic (i.e., Co/CoO)/nonmagnetic bilayers — i.e. \([\text{Co/CoO/Ag}]_{30}\) — and was prepared on a glass substrate and capped by an 8 nm Ag layer (further preparation details are given in our previous article \([12]\)). Each deposited (layer) quantity of Co and Ag corresponded to a nominal thickness of 5 nm (for the case of Co, this corresponds to the layer thickness that would be obtained under deposition in the absence of oxygen). As we explain below, a combination of x-ray reflectivity and magnetic data allows us to estimate the individual Co and CoO layer thicknesses in the magnetic bilayers.

Magnetic measurements, using a vibrating sample magnetometer, were carried out on the same multilayer sample following its (post-deposition) annealing at progressively higher temperatures \(T_{\text{ann}}\). For each \(T_{\text{ann}}\), the value of \(H_E\) was extracted from a hysteresis loop recorded immediately after field cooling (FC), i.e. the first \((n = 1)\) loop. The FC was performed with \(H = 10\) kOe applied parallel to the multilayer plane, cooling from room temperature to a temperature, \(T_{\text{cryo}}\) (the subscript ‘cryo’, which refers to cryostat, is used so as to distinguish this temperature from the annealing temperature, which is denoted using the subscript ‘ann’). The field cycling during each hysteresis loop acquisition was between (at most) +15 and \(-15\) kOe, again applied parallel to the plane. By choosing to use the \(n = 1\) loop to determine \(H_E\), we avoid any discrepancies (as a function of \(T_{\text{ann}}\)) due to training effects, which are known to be important for Co–CoO interfaces (see, for example \([13]\)).

Each annealing treatment was performed under vacuum (10\(^{-7}\) mbar), with the sample substrate in contact with a hot-plate held at a fixed temperature \(T_{\text{ann}}\) for a duration time \(t = 30\) min. X-ray reflectivity and diffraction (XRD) measurements were carried out (using Cu K\(\alpha\) radiation) on the same sample investigated in the magnetic studies. In order to investigate the in-plane crystallinity, a second multilayer from the same sample batch was studied, after identical thermal treatments, using the surface diffraction beamline SpLine (BM25) of the European Synchrotron Radiation Facility (ESRF).

The precise stoichiometry of the oxide layers in our multilayer sample was not established in our previous study \([12]\). Given that the oxygen pressure we have used in sample deposition is a factor of 20 less than the pressure (\(p_{O_2} = 4 \times 10^{-4}\) mbar) used in the preparation (again by reactive sputtering) of the CoO/Fe bilayers studied by Nowak \textit{et al} \([10]\), an oxide stoichiometry different from the overoxidized one (CoO\(_{1+\delta}\)) deduced by those authors may be expected for our sample. It is worth noting, however, that the Rutherford backscattering (RBS) technique, which was used by Nowak \textit{et al} \([10]\) to directly conclude CoO\(_{1+\delta}\) stoichiometry, was not employed in the present study because each Co/CoO bilayer in our (multilayer) sample was formed in a single deposition step and, thus, each oxide layer could not be separately studied, i.e. an RBS study would have observed a Co signal originating from both the Co and CoO layers, which would have led to difficulties when scaling that signal to the oxygen one in order to reliably determine the oxide stoichiometry. As it turns out, however, the oxide stoichiometry in our
sample can be deduced from the annealing dependence of the EB and other properties. This, indeed, will constitute the main conclusion of the present work.

In order to obtain complementary information on the annealing effect upon the morphology of the Co/CoO bilayers in the multilayer described above, multilayer samples of the form [Co/CoO]_8 (no Ag spacer layers) were also prepared for study. Each bilayer was obtained in the standard way, by first depositing a layer of Co in the absence of oxygen (again we used a nominal thickness of 5 nm) and then oxidizing the top part of it by introducing oxygen in the sputtering chamber (again using pO_2 = 2 × 10^{-5} mbar). As is well known in the literature, such an oxidation process results in an oxide layer with a maximum thickness of 2.5 nm [14]. The [Co/CoO]_8 multilayer samples were subjected to equivalent annealing treatments to those described above, and a specular x-ray reflectivity measurement (only) was taken between each individual annealing.

3. Results and discussion

Figure 1 shows the annealing dependence of the EB field. The inset on the left-hand side of the figure shows examples (for selected values of T_{ann}) of the (n = 1) hysteresis loops from which the values of H_E were extracted. Up to T_{ann} ≈ 300 °C (= T*) H_E is approximately constant, after which it begins to fall and becomes vanishingly small above around 500 °C. The coercive field H_C (not shown) varies with T_{ann} in a very similar way to H_E, implying that coercivity is due to exchange coupling in this system, as already established in our previous study [12].

The form of the H_E(T_{ann}) dependence is suggestive of a single thermally induced process controlling the value of H_E. If that process were the temperature variation of some structural parameter, Λ (with H_E ∝ Λ), which varied according to an Arrhenius relationship, Λ = Λ^0 exp(−τ t), where τ is the attempt frequency (= τ^0 exp[−E_A/(kT_{ann})]) and E_A is the activation energy, then the annealing dependence of the EB field would follow

\[ H_E(T_{ann}) = H_E^0 \exp \left\{- \frac{E_A}{kT_{ann}} \right\} t, \]  

where H_E^0 denotes the EB field prior to annealing. The solid line in figure 1 is a fit using equation (1), the fitted values of which are E_A = 0.8 eV and τ^0 = 2.0 × 10^2 s^{-1}. Of course, T_{ann} in the above equation is in Kelvin, whereas we have chosen to use °C in figure 1. Indeed, throughout we use units °C for the annealing temperature, T_{ann}, and K for the actual sample temperature, T_{cryo}, during a magnetic measurement, so as to avoid confusion. Also, we should note that because the thermal treatments were carried out on the same sample, at progressively higher temperatures, the use of equation (1) is an approximation, but is assumed to be a valid one.

Before specifying the structural property we ascribe to be the ‘EB control parameter’ (Λ), we discuss other experimental results. X-ray results are shown in figure 2. The specular (θ−2θ) x-ray reflectivity—panel (a)—comprises superlattice Bragg peaks due to the composite (Co + CoO) magnetic/nonmagnetic (Ag) bilayers present for all T_{ann} up to 500 °C. Fitting the

4 That is, since the same annealing time t (= 30 min) was employed for each treatment, and the difference between each temperature T_{ann} and the subsequent point T_{ann} + ΔT_{ann} is fairly large (ΔT_{ann} = (at least) 30 °C), our assumption is that each subsequent annealing of the multilayer (previously annealed to T_{ann}) to a new temperature of T_{ann} + ΔT_{ann} yields an approximately equal structural state (i.e. value of Λ) as that which would be attained if the as-deposited sample were treated for the same time (t) at T_{ann} + ΔT_{ann}. 

New Journal of Physics 10 (2008) 083028 (http://www.njp.org/)
Figure 1. Post-deposition annealing (at temperatures $T_{\text{ann}}$) dependence of the EB field, measured at a sample temperature $T_{\text{cryo}} = 80$ K. The solid line is a fit to the data using equation (1). Insets: (left) corresponding hysteresis curves for selected values of $T_{\text{ann}}$ and (right) the multilayer structure of the as-deposited sample, i.e. Ag (capping)/[Co/CoO/Ag]$_{30}$/substrate (glass).

data (using the LEPTOS package [15]) confirms that the thicknesses of the Ag and magnetic (Co + CoO) layers essentially do not vary with $T_{\text{ann}}$ (see inset). Due to the small contrast in electron density between Co and CoO compared to the contrast between Co (or CoO) and Ag, specular reflectivity from our multilayer is not sensitive to the morphology of the composite magnetic layers (we commented upon this in our earlier study [12]). However, essentially full segregation of Co and CoO occurs in the as-deposited multilayer, i.e. the (Co + CoO) magnetic layers were deduced, to all intents and purposes, to be Co/CoO bilayers [12] (see above). What is more, the reflectivity studies we have carried out on post-deposition annealed [Co/CoO]$_8$ (no Ag spacer layers) multilayer samples (results not shown) demonstrate that at least a temperature ($T_{\text{ann}}$) of $400$ °C is required to produce any degradation in the multilayer structure, whereas $H_E$ starts to fall at $300$ °C ($T^*$) in figure 1, suggesting that the thermally activated structural process that gives rise to the initial fall in $H_E$ in figure 1 is not a morphological one involving reorganization of Co and CoO regions within the magnetic layers. Furthermore, using the initial value of magnetic bilayer thickness ($\approx 8.5$ nm, see inset of figure 2(a)) along with the estimated fraction of the total number of deposited Co atoms initially in the F phase (see below), the initial thickness of the CoO layers in the multilayer studied in figure 1 may be estimated [12] to be $6.5$ nm, which is almost three times greater than the thickness of the CoO layers in the [Co/CoO]$_8$ (no Ag spacers) multilayers (see above). Thus, the minimum temperature ($T_{\text{ann}}$) of $400$ °C required to produce any degradation in the multilayer structure for the case of the [Co/CoO]$_8$ (no Ag spacers) multilayer samples is likely to be a conservative estimate when applied to the case of the multilayer studied in figure 1.

Figure 2(b) shows the XRD pattern of the as-deposited [Co/CoO/Ag]$_{30}$ multilayer acquired using laboratory x-rays and a standard $\theta$–$2\theta$ geometry (i.e. scattering vectors perpendicular to the multilayer plane). The most intense peak of the pattern is an Ag (002) reflection, which has a shoulder on its low $2\theta$ side, located around the (bulk) CoO (002) position,
Figure 2. (a) X-ray reflectivity and (b) out-of-plane and (c) in-plane XRD for selected values of $T_{\text{ann}}$. (a) and (b) were taken with laboratory x-rays ($\lambda = 1.54 \text{ Å}$) while (c) was measured using synchrotron radiation ($\lambda = 0.88 \text{ Å}$). The solid lines in (a) are fitting curves, and the inset shows the corresponding Ag layer and composite (Co/CoO) magnetic bilayer thicknesses. In (b), the positions of all possible reflections for the Ag, CoO and Co phases (all fcc) are shown, and the arrow indicates a CoO (002) signal, a close up of which is shown in the inset along with data for two selected annealings. The same CoO reflection is indicated by the arrow in (c).

indicating (since no other CoO signals are identified in the pattern) (002) textured CoO layers. It should be noted that the (100) position for (bulk) hcp Co is close to the CoO (002) position (so as not to have too many reflection bars in the figure, when the pattern itself is almost entirely due to diffraction from the Ag layers, the hcp Co positions have not been plotted). However, given that we have estimated (above) that the layer thickness of CoO is around three times that of the Co, it is reasonable to expect the intensity in the shoulder to be predominantly due to CoO. Indeed, we have not been able to determine, from this (as-deposited) XRD pattern, whether the sample contains Co in the hcp phase. Likewise, we have not been able to determine the presence of fcc Co, the (111) position of which, for example, is very close to the Ag (002) position (given that both the layer thickness and the atomic number ($Z$) of Ag are around twice the corresponding values for Co—see above—it is reasonable that the Ag (002) signal overshadows any possible trace of an fcc Co (002) reflection, a simple estimate for the ratio of the signal strengths being 16). Thus, qualitatively speaking, all the observed features in the as-deposited pattern can be accounted for by the Ag layers, except for the shoulder, which is attributed to the CoO layers.

New Journal of Physics 10 (2008) 083028 (http://www.njp.org/
With increasing $T_{\text{ann}}$, the $\theta$–2$\theta$ XRD from the sample does not present any marked differences from the as-deposited pattern. The shoulder peak, however, becomes increasingly sharper upon successive annealing above 300 °C ($= T^*$)—see the inset of figure 2(b). The evolution of its shape—see, for example, the slight asymmetry at 410 °C (inset)—also suggests the possibility of an increasingly non-negligible hcp Co (100) contribution, however, the data do not permit any useful quantitative (e.g. Rietveld) analysis to explore this possibility. On the other hand, fitting the intensity in the shoulder of the 500 °C pattern using a single Lorentzian (+ the tails of the Ag signal), a value of Scherrer (out of plane) grain size consistent with the estimated CoO layer thickness (see above) is obtained.

One possibility is that the changes in the shoulder peak above $T^*$—figure 2(b)—are related to an annealing-induced removal of defects from the AF layers. Since the crystallinity of thin (6.5 nm) CoO layers may be expected to be more extended in the plane than perpendicular to it (the latter being the direction probed by the scans in panel (b)), a logical way to investigate such a possibility is by means of an in-plane XRD study. Such an experiment was carried out (Spline, ESRF), which involved working at fixed, grazing incidence and exit angles ($= 2^\circ$ measured vertically from the sample surface), and scanning the detector horizontally in order to register diffraction signals. Figure 2(c) shows in-plane patterns for selected values of $T_{\text{ann}}$, taken around the position of the Ag (002) reflection, where again a shoulder is present at the CoO (002) position. However, this time the shape of the shoulder peak above $T^*$ suggests the signal to be entirely due to CoO (i.e. a negligible hcp Co (100) contribution). One observes that the position of this oxide signal shifts to lower 2$\theta$ with increasing $T_{\text{ann}}$ ($> T^*$), and the signal becomes sharper. The variation of the CoO peak width (full width at half maximum (FWHM)) and lattice parameter, determined from double Lorentzian profile fits to the (in-plane) patterns around the Ag (002) position, is shown in figure 3(c).

It should be noted that in the study by Nowak et al [10], a similar shift to lower 2$\theta$ was observed for a CoO XRD peak with increasing substrate temperature from 250 to 450 °C—the reflection in their case being a (111) measured in the standard $\theta$–2$\theta$ geometry—and the effect was attributed to a reduction in lattice compression (macro strain [16]). However, the in-plane Ag lattice parameter (determined from the fitted position of the Ag peak in figure 2(c)) does not vary in the same, monotonic way above $T^*$ as the CoO lattice parameter (figure 3(a)), thus casting doubt on any interpretation of our CoO peak shift in terms of a release of lattice compression. As we now discuss, the shift in our CoO peak width (full width at half maximum (FWHM)) and lattice parameter, determined from double Lorentzian profile fits to the (in-plane) patterns around the Ag (002) position, is shown in figure 3(c).

Figure 3(b) shows the $\mu_S(T_{\text{ann}})$ dependence, which is approximately constant up to $T_{\text{ann}} = T^*$ but increases upon annealing above $T^*$. One plausible interpretation of this behaviour is that the amount of the F (Co) phase in the multilayer in some way increases with increasing $T_{\text{ann}} > T^*$. A possible mechanism causing this effect is diffusion of an excess of cobalt ions ($\delta$) out of the AF layers and into the F layers, which could occur if the cobalt oxide layers are, initially, slightly underoxidized, i.e. the stoichiometry is CoO$_{1-\delta}$ $\equiv$ Co$_{1+\delta}$O for small $\delta$. The activation energy ($E_A = 0.8$ eV) corresponding to the fit using equation (1) in figure 1 is certainly consistent with calculated values ($\approx 1$ eV) for self-diffusion of Co$^{2+}$ ions through (bulk) CoO [17]. In the study by Nowak et al [10], it was diffusion (removal) of surplus oxygen from the CoO layer—i.e. an elimination of O substitutional point defects—which was used to explain the variation in the EB properties upon annealing, and such an effect is associated with
Figure 3. Annealing dependence of (a) the lattice parameter—right axis—and the FWHM—left axis—corresponding to the in-plane CoO XRD peak; (b) the room temperature saturation magnetic moment; and (c) the EB onset temperature. The solid lines in the three panels were derived from the fit of $H_E(T_{\text{ann}})$ in figure 1—see equations (2) and (3) for the cases of the (red) lines in (a) and (b), respectively. Insets: (b) hysteresis loops recorded at $T_{\text{cryo}} = 300$ K and (c) the temperature dependence of the EB field for selected values of $T_{\text{ann}}$, where the solid line is a fit to the $T_{\text{ann}} = 470$ °C data using a Brillouin function with $J = 5/2$. (Note: although the subscript ‘cryo’ is used to label the measurement temperature in (b), the sample was not mounted in the cryostat during the acquisition of these (room temperature) data.)
a higher activation energy than the Co\textsuperscript{2+} diffusion that we propose here [17] (cf annealing at 1100 °C was required to cause the O\textsuperscript{2−} diffusion [10], which is much higher than the maximum temperature in figure 1 of the present paper).

However, up to now in the literature, only the Co\textsubscript{1−δ}O stoichiometries of cobalt oxide—ranging from Co\textsubscript{2}O\textsubscript{1} (δ = 0) to CoO\textsubscript{4} (δ = 0.25)—have been discussed in relation to EB systems [6, 9, 10, 18]. Indeed, those stoichiometries are the stable cobalt oxides [19]. It is possible, however, that the reactive sputtering of Co at the relatively low oxygen pressure used in the present study (significantly lower than that which resulted in Co\textsubscript{1−δ}O layers in the Nowak et al study [10], see above) could have produced layers of the unusual CoO\textsubscript{1−δ} stoichiometry. The following data analysis supports this idea.

Assuming that any excess Co ions in the AF layers will make a negligible contribution to the initial magnetic moment, μ\textsubscript{S}\textsuperscript{0}, in figure 3(b), and that once these ions were to migrate into the adjacent F layers, each newly arrived atom will contribute an equivalent moment to the total moment (μ\textsubscript{S}) as each of the atoms originally present in the F layers, then the fractional change in μ\textsubscript{S} between 300 °C (≈ T\textsuperscript{*}) and 500 °C—namely Δμ\textsubscript{S}/μ\textsubscript{S} = 0.17—may be used to determine an estimate for what the initial (T\textsubscript{an} < T\textsuperscript{*}) Co excess fraction (δ\textsuperscript{0}) would be. That is, Δμ\textsubscript{S}/μ\textsubscript{S} will simply be equal to the fractional change in the number of Co ions in the F phase (Δf\textsubscript{Co:F}). The corresponding fractional change for the AF phase is given by Δf\textsubscript{Co:AF} = −(F\textsubscript{Co:F}/F\textsubscript{Co:AF}) Δf\textsubscript{Co:F} = −0.1, where F\textsubscript{Co:F} (= 0.36) and F\textsubscript{Co:AF} (= 0.64 = 1 − F\textsubscript{Co:F}) are the estimated fractions of the total number of deposited Co atoms initially in the F and AF phases, respectively\textsuperscript{5}. Since the initial value for the Co excess factor (δ\textsuperscript{0}) is expected to be small, the value of Δf\textsubscript{Co:AF} may be approximated\textsuperscript{6} to that of Δδ, which denotes the change in the value of δ from its as-deposited value to its value at 500 °C, i.e. Δδ ≈ −0.1. Assuming the AF layers approach the 1 : 1 (Co\textsubscript{1}O\textsubscript{1−δ}) stoichiometry as T\textsubscript{an} → 500 °C, the value of Δδ implies an initial AF layer stoichiometry of CoO\textsubscript{0.9}, i.e. Co\textsubscript{1−δ}O\textsubscript{δ} layers, with δ = 0.1, in the as-deposited multilayer. Remarkably, expressing now the (in-plane) lattice parameter for the oxide layers using a Vegard law, whereby an excess δ of Co ions occupies oxygen sites in the fcc structure of CoO—i.e. a\textsubscript{CoO\textsubscript{1−δ}} = a\textsubscript{Co} + δ + a\textsubscript{Co} (1 − δ) = a\textsubscript{CoO} − δ(a\textsubscript{CoO} − a\textsubscript{Co})—and taking the value of a\textsubscript{CoO} as that for its fcc phase, an identical initial value of δ (= 0.1) is deduced from the total variation in this lattice parameter—see arrows on right axis in figure 3(a).

Considering now the case of δ being the EB structural control parameter—i.e. H\textsubscript{E}(T\textsubscript{an}) ∝ δ(T\textsubscript{an})—and denoting by C the constant of proportionality linking the two parameters, then one expects (by rewriting the above Vegard expression in terms of H\textsubscript{E} and C) the in-plane CoO lattice parameter to follow

\[ a_{CoO_{1−δ}}(T_{an}) = a_{CoO} - \frac{H_{E}(T_{an})}{C}[a_{CoO} - a_{Co}] \]

and the saturation magnetic moment (following some algebra\textsuperscript{7}) to be given by

\[ \mu_{S}(T_{an}) = \mu_{S}^{0}[1 - \frac{F_{Co:AF}}{F_{Co:F}} C(H_{E}(T_{an}) - H_{E}^{0})]. \]

\textsuperscript{5}The value of F\textsubscript{Co:F} was determined by comparing the initial value of μ\textsubscript{S} in figure 3(b) with the value of μ\textsubscript{S} for a multilayer prepared identically but for an absence of oxygen in the sputtering chamber.

\textsuperscript{6}Denoting the initial value of δ by δ\textsuperscript{0}, the fractional change Δf\textsubscript{Co:AF} = Δδ/(1 + δ\textsuperscript{0}) ≈ Δδ for small δ\textsuperscript{0} (≤ 01).

\textsuperscript{7}μ\textsubscript{S}(T_{an}) = μ\textsubscript{S}^{0}[1 + Δf\textsubscript{Co:F}(T_{an})] = μ\textsubscript{S}^{0}[1 − (F\textsubscript{Co:F}/F\textsubscript{Co:AF}) Δf\textsubscript{Co:AF}(T_{an})] ≈ μ\textsubscript{S}^{0}[1 − (F\textsubscript{Co:AF}/F\textsubscript{Co:F}) Δδ(T_{an})] = μ\textsubscript{S}^{0}[1 − (F\textsubscript{Co:AF}/F\textsubscript{Co:F})(δ(T_{an}) − δ\textsuperscript{0})], and equating the initial δ value (δ\textsuperscript{0}) to H\textsubscript{E}/C.

\[ = \mu_{S}^{0}[1 - \frac{F_{Co:AF}}{F_{Co:F}} C(H_{E}(T_{an}) - H_{E}^{0})]. \]

\[ H_{E}(T_{an}) \sim \delta(T_{an}) \]

New Journal of Physics 10 (2008) 083028 (http://www.njp.org/)
The curves (red lines) drawn through the lattice parameter and $\mu_S$ data points in figure 3 were made using precisely these (respective) equations, with $H_E(T_{ann})$ being the fit in figure 1 and $C = 25$ kOe (for both panels)\(^8\). This self consistency between the three parameters—$H_E$, $a_{CoO}$, and $\mu_S$—is strongly supportive of the proposed initial underoxidized stoichiometry in the AF layers, whereby $\delta$ acts as the main EB control parameter in the multilayer system.

The reduction in the FWHM of the CoO peak—figure 3(a)—is an effect expected to accompany the change in stoichiometry proposed above, i.e. both an increase in the in-plane grain size and a reduction in the micro-strain may occur upon removal of substitutional defects from the oxide layers, and both effects will give rise to a reduction in FWHM [16]. Of course, in order to separate both effects—i.e. determine both the in-plane crystallite size and strain contributions to each value of FWHM in figure 3(a)—multiple diffraction peaks from the CoO phase (for each $T_{ann}$) would be required [16], whereas only one peak is available from our synchrotron XRD study. The curve (black line) drawn through the values of FWHM—figure 3(a)—is again (as for the lattice parameter) a transformed version of the $H_E(T_{ann})$ fit in figure 1.

Further evidence supportive of the proposed change in stoichiometry is provided by the increase in the EB onset temperature, $T_{OE}$, for $T_{ann} > T^*$—figure 3(c)—since it is expected that departure from the Co$_{1/2}$O stoichiometry (or, equivalently speaking, the presence of defects in the AF component) will reduce the Néel temperature $T_N$, and $T_N$ fixes the upper limit of $T_{OE}$ [6, 10]. Furthermore, the curve drawn through the $T_{OE}$ data points is again a transformed version of the $H_E(T_{ann})$ fit. It is also remarkable how $T_{OE}$ approaches the value of $T_N$ for bulk CoO (293 K) as $T_{ann}$ approaches 500 °C. Moreover, the form of the $H_E(T_{cryo})$ dependence—inset of figure 3(c)—tends toward that of a Brillouin function with $J = 5/2$ for increasing $T_{ann} > T^*$, again supportive of a reduction in defects in the AF component [20].

The role of roughness at the F–AF interfaces on the EB properties should also be considered [2, 22]. Some reduction in roughness upon annealing up to 500 °C—the temperature at which most of the initial EB field has been lost in figure 1—might be expected. However, as we have discussed above (and in [12]), the presence of the Ag spacer layers in the multilayer structure results in the x-ray (specular) reflectivity being insensitive to changes in the morphology of the Co/CoO bilayers. Indeed, all of the reflectivity curves in figure 2(a) were fitted using the same value for roughness at the Co–CoO interfaces. Notwithstanding this problem, the work by Nowak et al [10] suggests that even a significant roughness reduction at the F–AF interfaces (as achieved in their annealing up to 1100 °C) would not be expected to produce the remarkable change in EB properties that we observe in figures 1 and 3(c).

Specifically, Nowak et al demonstrated that the effect (on EB properties) of a removal of substitutional point defects from the CoO layer (in their case, defects due to an oxygen surplus) via the sample annealing to 1100 °C far outweighed the effect of the reduction in roughness at the AF–F interface.

Of course, our proposed mechanism of Co diffusion into the F layers implies an increase in the thickness ($t_F$) of these layers. However, since this thickness increase will be small, its effect on the value of the EB field (via the $H_E \propto 1/t_F$ relation [23]) is understood to be secondary compared to the effect due to the proposed change in stoichiometry of the AF layers.

---

\(^8\) This value should be considered as being an average over the investigated $\delta$ range, i.e. $C = (1/0.1) \int_0^{0.1} (\partial H_E/\partial \delta) \, d\delta$.

\(^9\) $J = 5/2$ is consistent with the experimental values of magnetic moment for Co$^{2+}$ in various salts; see, for example [21].
For example, up to $T_{\text{ann}} = 400^\circ$C the relative change in the saturation magnetic moment (figure 3(b)) is only around 8% of the initial value. Thus, the associated F thickness change will also be (only) around 8%, which will give rise to only a 7% decrease in the EB field (via $H_E \propto 1/t_F$), whereas the observed reduction (up to 400 $^\circ$C) in figure 1 is around 60%.

Thus, we attribute the EB properties of the present multilayer, at least for post-deposition annealing up to 400 $^\circ$C (see above), to be due (mainly) to an excess of Co in the AF layers, which gives rise to a (AF) domain state (and concomitant uncompensated spins), yielding a scenario similar to those reported earlier from studies involving a defective AF component [6]–[11]. In other words, we conclude that the initial reduction in the EB field (figure 1) is due mainly to a decrease in the value of the Co excess fraction ($\delta$) in the AF layers. That this reduction takes place beginning from an initial value of 0.1 ($= \delta^o$) may be considered as qualitatively consistent with the analysis by Hong et al [7], who studied the case of non-magnetic impurities in CoO layers. That is, the curve showing the fraction of uncompensated spins as a function of (Mg) doping factor determined by those authors exhibits a maximum positioned at a value of doping fraction just greater than 0.1. Thus, for the hypothetical case of an as-deposited multilayer containing non-stoichiometric CoO layers with a Co excess fraction $\delta^o > 0.1$, one might expect an initial increase in the EB field upon annealing, as $\delta$ initially decreased towards the value at which the uncompensated spin density was maximum.

It would be interesting to attempt to probe the uncompensated spins in the proposed Co-rich AF layers as a function of (post-deposition) annealing, at least up to 400$^\circ$C. To this end, however, the application of the thermoremanent magnetization technique [5, 8] would be hampered by an unavoidable combination of signals from both Co (F) and CoO (AF) layers, since, as noted above, each AF layer is formed in the same deposition step as a F layer. On the other hand, polarized neutron reflectometry could offer a valuable method to probe the uncompensated spins [24]. Likewise, to confirm (directly) the proposed AF layer stoichiometry (avoiding the problems which would be incurred using the RBS method—see above), hard x-ray photoelectron spectroscopy (HAXPS) could prove valuable, since the technique is depth-dependent with a resolution better than the estimated initial CoO layer thickness ($= 6.5 \text{ nm}$, see above) [25].

It should be noted, finally, that the complete suppression of the EB effect observed upon annealing up to 600$^\circ$C (figure 1) is not entirely attributed to the Co diffusion mechanism (removal of defects from the AF layers), since, for example, even if all the (Co) substitutional defects were eliminated from the AF layers at $T_{\text{ann}} = 600^\circ$C, interface roughness [2] and finite (in plane) grain size [4] would still be expected, resulting in some measurable EB effect. In fact, the superlattice Bragg peaks observed in the reflectivity—figure 2(a)—begin to degrade at $T_{\text{ann}} > 500^\circ$C (not shown), thus, it is reasonable to attribute the disappearance of the EB effect to an additional process involving coarsening of the Co and CoO components of the magnetic layers (immiscible phases in equilibrium), resulting in the presence of F–AF interfaces perpendicular to the plane, with correspondingly large effective F layer thicknesses (cf $H_E \propto 1/t_{\text{eff}}$ [23]). Indeed, this coarsening process may even begin at a temperature less than 500$^\circ$C but not below 400$^\circ$C, since the reflectivity study of the [Co/CoO]$_8$ (no Ag spacers) multilayers (see above) found the initial structure to be preserved up to the latter temperature. As such, the value of the proportionality constant $C = 25 \text{ kOe}$ (above) should be taken as being an upper limit value, since, in its determination, it is assumed that the variation in the Co excess factor ($\delta$) is the only quantity controlling the value of $H_E$ up to 500$^\circ$C. The fact (as commented above) that the Co diffusion mechanism will give rise to a small increase in the
F layer thickness, and, thus, a concomitant reduction in \( H_E \), also implies that \( C = 25 \text{ kOe} \) is an upper limit.

4. Conclusions

The effect (on EB properties) of non-stoichiometry of the form \( \text{CoO}_{1+\delta} \) (i.e. overoxidation) in the AF component has already been reported in the literature [6, 9, 10]. Here, we have presented a comprehensive study on the (post-deposition) annealing effect on EB and other properties of a \([\text{Co/CoO/Ag}]_{30}\) multilayer prepared by reactive sputtering, the results of which have allowed us to conclude AF layers of the unusual \([19] \text{CoO}_{1-\delta}(=\text{Co}_{1+\delta}\text{O})\) stoichiometry, with \( \delta = 0.1 \) for the as-deposited sample. Thus, it is assumed that a Co excess (\( \delta \)) in the AF layers plays a role akin to impurity atoms—both nonmagnetic [6]–[8] and magnetic [11]—and excess oxygen [6, 9, 10] in the AF component in previous studies, namely by producing an enhanced EB effect via uncompensated spins associated with substitutional point defects. An alternative way of expressing this conclusion, however, is to state that we have exploited the sensitivity of the EB properties to defects in the AF component in order to infer—by corroboration with other structural and magnetic characterization—that, initially, the oxide layers have this unusual \((\text{CoO}_{1-\delta})\) stoichiometry. The annealing behaviour of the saturation magnetic moment—figure 3(b)—has been a crucial piece of evidence leading us to this conclusion, i.e. an annealing-induced diffusion of a Co excess out of the AF and into the F layers has allowed us to account for the rise in \( \mu_S \) in figure 3(b).

It is hoped that the present work will encourage similar annealing studies whereby defects in the AF component of an EB system are eliminated gradually—i.e. via multiple annealing steps—rather than in a single step, as was the case in the limited number of reports available in this area [10, 26]. In this way, the thermal metastability of such defects may be best exploited in order to further investigate the role of defects in exchange-biased systems.

Acknowledgments

We acknowledge financial support from the JCLM (project GC-02-009). We thank M Rivera and E Prado for their expert technical support in the sample preparation and annealing. We also thank M E Medina and G R Castro for their invaluable assistance in the synchrotron experiment.

References

[1] Nogués J, Sort J, Langlais V, Skumryev V, Suriñach S, Muñoz J S and Baró M D 2005 Phys. Rep. 422 65
[2] Berkowitz A E and Takano K 1999 J. Magn. Magn. Mater. 200 552
[3] Kuch W, Chelaru L I, Offi F, Wang J, Kotsugi M and Kirschner J 2006 Nat. Mater. 5 128
[4] Bode M, Vedmedenko E Y, Von Bergmann K, Kubetzka A, Ferriani P, Heinze S and Wiesendanger R 2006 Nat. Mater. 5 477
[5] Marti DJ, Berkowitz A E and Smith DJ 1999 Appl. Phys. Lett. 74 1314
[6] Takano K, Kodama R H, Berkowitz A E, Cao W and Thomas G 1997 Phys. Rev. Lett. 79 1130
[7] Miltényi P, Gierlings M, Keller J, Beschoten B, Güntherodt G, Nowak U and Usadel K D 2000 Phys. Rev. Lett. 84 4224
[8] Hong J-I, Leo T, Smith D J and Berkowitz A E 2006 Phys. Rev. Lett. 96 117204
[9] Fecioru-Morariu M, Ali S R, Papusoi C, Sperlich M and Güntherodt G 2007 Phys. Rev. Lett. 99 097206
[9] Ghadimi M R, Beschoten B and Güntherodt G 2005 Appl. Phys. Lett. 87 261903
[10] Nowak G, Remhof A, Radu F, Nefedov A, Becker H and Zabel H 2007 Phys. Rev. B 75 174405
[11] Ali M, Marrows C H and Hickey B J 2008 Phys. Rev. B 77 134401
[12] Normile P S, De Toro J A, Muñoz T, González J A, Andrés J P, Muñiz P, Galindo R E and Riveiro J M 2007 Phys. Rev. B 76 104430
[13] Brems S, Temst K and Van Haesendonck C 2007 Phys. Rev. Lett. 99 067201
[14] Radu F, Etkorn M, Siebrecht R, Schmitte T, Westerholt K and Zabel H 2003 Phys. Rev. B 67 134409
[15] Ulyanenkov A 2006 Appl. Surf. Sci. 253 106
[16] Cullity B D and Stock SR 2001 Elements of X-Ray Diffraction 3rd edn (Englewood Cliffs, NJ: Prentice Hall)
[17] Mrowiec S and Przybylski K 1977 Oxidation of Metals vol 11 (Netherlands: Springer) p 383
[18] Laureti S, Agostinelli E, Scavia G, Varvaro G, Rossi Albertini V, Generosi A, Paci B, Mezzi A and Kaciulis S 2008 Appl. Surf. Sci. 254 5111
[19] Dieckmann R 1977 Z. Phys. Chem. 107 189
[20] Fitzsimmons M R, Leighton C, Hoffmann A, Yashar P C, Nogués J, Liu K, Majkrzak C F, Dura J A, Fritzsche H and Schuller I K 2001 Phys. Rev. B 64 104415
[21] Blundell S 2001 Magnetism in Condensed Matter (New York: Oxford University Press)
[22] Malozemoff A P 1987 Phys. Rev. B 35 3679
[23] Polisetty S, Sahoo S and Binek C 2007 Phys. Rev. B 76 184423
[24] Roy S et al 2005 Phys. Rev. Lett. 95 047201
[25] Rubio-Zuazoa J R and Castro G R 2005 Nucl. Instrum. Methods Phys. Res. A 547 64
[26] Moran T J, Gallego J M and Schuller I K 1995 J. Appl. Phys. 78 1887

New Journal of Physics 10 (2008) 083028 (http://www.njp.org/)