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Interdiffusion and magnetic properties of $Gd_{1-x}Co_x$/Co multilayers

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Abstract

The interdiffusion process in $Gd_{1-x}Co_x$/Co multilayered systems has been investigated, in several series of samples made by sputtering, with different values of the Co content in the alloy (x). Grazing-incidence x-ray profiles and the electrical resistivity, together with magnetic measurements at room temperature, allow us to monitor and quantify the interdiffusion between layers as well as their magnetic properties. It is shown that this interdiffusion occurs on increasing the Co content of the alloy layer up to around 60% Co. In the $x = 0.60$ series the interdiffusion was found to be negligible and therefore a very good structure was obtained, while the ferrimagnetic structure between layers is preserved. The improved multilayered structure obtained in this system could lead to the development of new technological applications.

1. Introduction

For over 20 years, rare earth–cobalt alloys and multilayers have been considered interesting systems from a fundamental point of view, and also for magneto-optic applications. The magnetic behaviour of these alloys is ruled by the underlying antiferromagnetic (AF) exchange interaction between a ferromagnetic heavy rare earth (such as Gd) and a ferromagnetic transition metal (Fe, Co), which makes them ferrimagnetic. As regards the $Gd_{1-x}Co_x$ system, its magnetic properties are well established (see for example [1]). At room temperature (RT), these alloys do not show a magnetic moment up to about $x = 0.53$. For higher Co content, the magnetization rapidly increases up to a maximum around $x = 0.61$. Due to the difference in temperature dependence of the magnetization between Gd and Co atomic sublattices, three different magnetic states are allowed at RT. For $x < 0.80$ the magnetization state is dominated by the Gd sublattice (Gd-aligned state), a Co-aligned state occurs for $x > 0.80$, and finally a compensation of the total magnetization of the alloy can appear for x around 0.80, with

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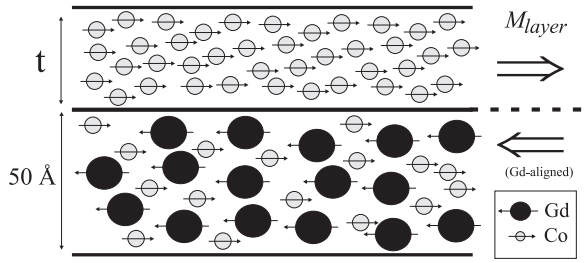

Figure 1. A schematic outline of the artificial 'giant' ferrimagnetic structure that appears in the $[Gd_{1-x}Co_x/Co]$ multilayers.

values of M near zero. In the case of Gd/Co multilayers, the exchange interaction at the interfaces converts these samples into 'giant' artificial ferrimagnets at temperatures below the Curie temperature of Gd ($T_c = 293$ K).

Always important in artificially structured systems, interdiffusion acquires a special relevance in the Gd/Co multilayered system due to the rapid interdiffusion and amorphization process that takes place [2,3]. For very thin layers, the effect is dramatic, impeding the growth of real multilayered structures. Very recently, a few works on the structural characterization of Gd/Co multilayers have appeared [4] but its grazing-incidence x-ray (GIXR) profiles clearly show the difficulty that obtaining a well defined structure entails. On the other hand, a similar magnetic structure can be obtained for $Gd_{1-x}Co_x/Co$ multilayers with a $Gd_{1-x}Co_x$ alloy (amorphous in a wide range of x) in the Gd-aligned state ($x < 0.80$), so they will share these interesting magnetic features (schematically outlined in figure 1). Nevertheless, interdiffusion in $Gd_{1-x}Co_x/Co$ multilayers has not been studied for $x \neq 0$ yet.

We have performed this study for different alloys with appropriate values of x in the range of the Gd-aligned state, in order to maintain the same magnetic structure of the Gd/Co multilayers. The series studied were: $[Gd_{50}/Co_t]_{20}$ and $Co_t[(Gd_{1-x}Co_x)_{50}/Co_t]_{12}$, with $x = 0.37$ and 0.60, and t ranging from a few to a hundred ångströms. In order to prevent oxidation, the multilayers were deposited following a sequence which was always finished with a last layer of Co. In addition to the series with $x = 0$ (an important reference, referred to as the '*pure*' series), $x = 0.37$ was chosen because previous studies on Gd/Co multilayered systems showed an enrichment of Gd layers near this characteristic value [5, 6], where the $Gd_{1-x}Co_x$ phase diagram has a deep eutectic point. For this reason this series will be referred to as '*eutectic*'. In order to investigate whether this concentration actually sets a limit for the interdiffusion process, we have also grown a series with $x = 0.60$. From the study of RT magnetization, electrical resistivity, x-ray diffraction (XRD), and GIXR profiles (in specular configuration, θ–2θ), we have deduced different degrees of this interdiffusion for the three series, that reach negligible values for $x = 0.60$.

2. Experimental details

The samples were fabricated by r.f. magnetron sputtering on glass substrates whose temperature was kept at RT during growth. The background pressure in the chamber was 6×10^{-7} mbar, and the deposition was performed in 99.999% pure Ar atmosphere with a partial pressure of 3.0×10^{-3} mbar. The different alloys employed were obtained by attaching the appropriate number of little pieces of Co (99.99%) to the Gd (99.9%) target. The composition of the alloys was determined by energy-dispersive x-ray microanalysis (EDAX) using a Philips XL-30

scanning electron microscope (SEM), on single films of alloys grown under the same conditions as the multilayers. No evidence of any significant contamination was found. Values given for compositions are within a typical 1% error. The deposition time is controlled by means of computerized shutters. The deposition rates employed in the experiment were about 5.7 Å s^{-1} for Gd and GdCo alloys, and 1.2 Å s^{-1} for Co. They were determined by quantifying the thickness of reference thin layers (about 300 Å thick) from the spacing between Bragg peaks in their low-angle x-ray reflectivity curves. The magnetic properties were measured with a vibrating-sample magnetometer (VSM) with fields up to 15 kOe applied in the film plane. XRD and GIXR profiles were taken using the usual specular configuration in a Philips X'pert-MPD system equipped with a Cu Kα radiation tube. For the resistivity measurements, a dc method and a four-point configuration were employed by means of pressure contacts.

3. Results and discussion

As a preliminary structural study, GIXR profiles were taken for some samples of each series. In figure 2 we show those corresponding to $t = 7$ Å for the three series studied in this work. These multilayers should be the worst as regards the definition of the periodicity, due to its low Co thickness. One readily notices the improved periodicity of the *eutectic* sample, with up to four clear Bragg peaks, also observed for the corresponding sample of the $x = 0.60$ series. The *pure* sample seems to be actually a modulated alloy, as is confirmed by the mathematical fits to the 7 Å scans also presented in figure 2. They yield roughness values between 8 and 9 Å, bigger than the Co thickness, for the *pure* sample, while the values remained around 4 Å for the others. Therefore, the effects of interdiffusion take special importance for these low values of Co thickness. On the other hand, for $t = 50$ Å, a clear periodic structure is revealed even in the *pure* sample, as shown in the inset of figure 2, which allows us to consider them as real multilayers in the general discussion. The modulation period of these samples can be readily obtained from the spacing between the Bragg peaks of the structure. Its analysis confirms modulation periods very near the nominal values, all within a 5% error. Initial results from polarized neutron reflectivity (PNR) on some of these samples have already been published [7] and also support modulation values near the nominal ones, with a reduced thickness of the Co layer due to interdiffusion. The unavoidable oxidation of the samples was confirmed to be limited to an upper layer of Co_2O_3 around 15 Å thick.

The RT values of the magnetic moment per layer and area unit (σ), for every sample studied, are shown in figure 3 as a function of the nominal Co thickness. Without interdiffusion, the behaviour expected would follow a straight line, its slope being equal to the magnetization of pure Co. The intersection with the t-axis would be at zero if the alloy employed had its T_C below RT, and otherwise positive as the alloy layer would shift the curve down on the σ-axis due to the ferrimagnetic coupling with the Co layers. For our samples, the expected linear increase of σ is observed above characteristic t-values. At low t, however, two of the σ versus t curves show a maximum. This behaviour can be explained, taking for example the *pure* ($x = 0$) series, as follows: the first sputtered Co fully diffuses into the alloy layer; this Co enrichment makes σ increase as expected for $Gd_{1-x}Co_x$ alloys [1] with x between 0.53 and 0.61, reaching a maximum at a thickness that we will call Δ. We interpret this as showing that interdiffusion stops above Δ because a stable alloy has been formed, and pure Co begins to grow on this compositionally modified $Gd_{1-x}Co_x$ alloy. The magnetic moments of this Co layer oppose those of the alloy layers (which are in a Gd-aligned state). As the contribution of alloy layers is not further increased, this makes σ decrease to a thickness (t_{comp}) for which the magnetic *compensation of the multilayer* occurs. For $t > t_{comp}$, Co layers dominate magnetically, as has been confirmed by magneto-optic Kerr effect (MOKE) curves taken for these samples [8], and

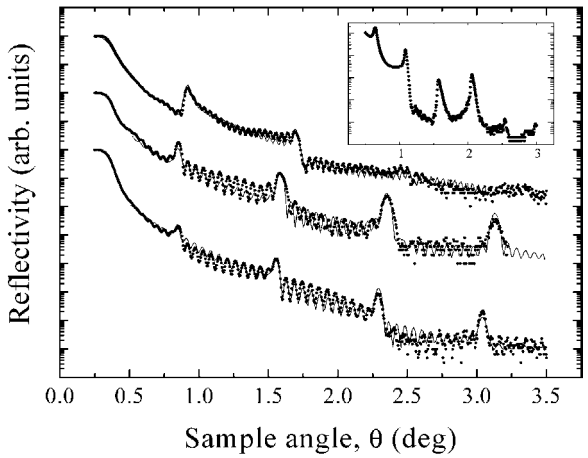

Figure 2. GIXR reflectivity as a function of the sample angle (θ) for the samples with $t = 7$ Å in the different series studied. The upper curve corresponds to the *pure* ($x = 0$) series, the middle one to the *eutectic* ($x = 0.37$), and finally the lower one to the $x = 0.60$ series. The curves have been shifted on the logarithmic y-axis (reflectivity) for the sake of clarity. Solid curves represent the best mathematical fits obtained in each case (see the text). The inset displays the experimental scan for $[Gd_{50}/Co_{50}]_{20}$.

Table 1. Summary of the values obtained for the amount of Co diffused into the alloy layer (Δ) and thicknesses of compensation of magnetization (M) in the multilayers (t_{comp}). The values obtained in this work (magnetization) are compared with those extracted from MOKE experiments [7].

	Magnetization			MOKE	
Series, x	Δ (Å)	t_{comp} (Å)	Slope (emu cm^{-3})	Δ_{MOKE} (Å)	t_{comp} (Å)
0	18	27	930	19	25–30
0.37	9	21	1180	8	20–21
0.60	0	17	1152	0	12–17

the linear increase of σ, expected when no Co atoms are lost by interdiffusion, is reproduced. The values of the slopes in this linear region of the σ–t curves, shown in table 1, coincide with those obtained for a series of pure Co layers of different thicknesses grown in the same conditions (1170 emu cm^{-3}), and are about 20% lower than the values for pure Co bulk, as usual for thin films, even if grown at ultrahigh vacuum [9]. The slightly lower value for the *pure* series indicates a higher degree of inhomogeneity in this case. This can be explained by broader interfaces, created because once Co atoms have entered into the crystalline Gd (or amorphous $Gd_{1-x}Co_x$ alloy) layer due to interdiffusion, it is easier for them to diffuse through an amorphous layer than through the crystalline counterpart. In a metal–metal amorphous system like ours, there is a large free volume available for diffusion in the form of voids in the glass structure; that act as of proto-vacancies of a sort [10]. In the crystalline case, diffusion of large atoms, usually termed *substitutional diffusion*, occurs mainly through grain boundaries, whose structural properties are closer to those of the amorphous material.

There remains a detail of figure 3 that deserves additional explanation. The possibility of σ decreasing between Δ and t_{comp}, as a result of further enrichment of the alloy layers (above $x = 0.61$), which would lead to a minimum of σ due to the *compensation of the alloy*, can be discarded thanks to the amorphous character of the $Gd_{1-x}Co_x$ alloy and its high resistivity.

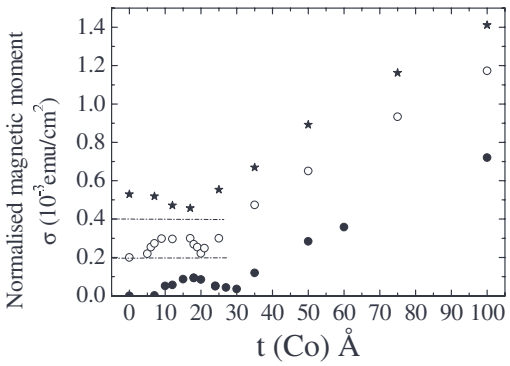

Figure 3. Magnetic moment per layer and area unit at RT for all the samples studied here, as a function of the thickness of the Co layer (t): $x = 0$ (lower, full circles), $x = 0.37$ (middle, open circles), $x = 0.60$ (upper, stars). The values displayed on the σ-axis correspond to the $x = 0$ series, while *eutectic* and $x = 0.60$ values have been vertically shifted by 0.2 and 0.4 respectively for clarity.

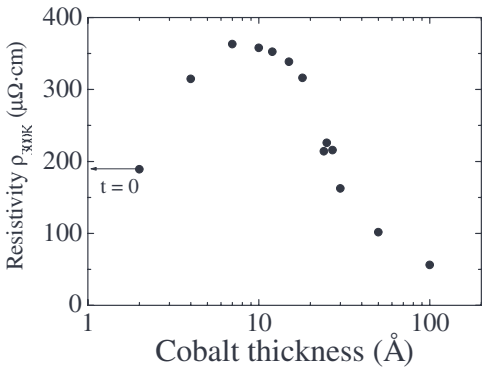

Figure 4. Electrical resistivity at RT for the samples of the *pure* ($x = 0$) series as a function of the thickness of the Co layer (t).

The growth of pure (nanocrystalline) Co has been detected from a sharp fall of the RT electrical resistivity of this samples. In figure 4 one of these curves corresponding to the *pure* series is presented, with a clear fall between 18 and 25 Å, very close to the $\Delta = 18$ Å value extracted from the *pure* curve in figure 3. Also, in figure 4, the amorphization process is revealed by a substantial increase of resistivity for low thickness values.

A similar discussion applies for the data corresponding to the *eutectic* series, also shown in figure 3. A lower value for Δ was found (only 9 Å), that indicates a lower degree of interdiffusion when this alloy is employed instead of pure Gd. Although this was already pointed out by Andrés *et al* [5], it has not been clear up to now whether this composition was actually that of the most stable amorphous alloy as regards interdiffusion. The fact that $\sigma \neq 0$ at RT for the thinner *pure* samples ($t < \Delta$) tells us that interdiffusion cannot finish near $x = 0.37$, because this alloy has $T_c <$ RT, so no maximum would be expected in the σ versus t curves for these series, only a linear increase. In contrast with this, the $x = 0.60$ series does not show any maximum; therefore pure Co should grow almost from the beginning. For low t the Co layers reduce the total σ of the sample, to bring it to multilayer compensation. The values for Δ and t_{comp} are summarized in table 1. These values for the amount of Co diffused

in the different series are in quite good agreement with those deduced from the study of MOKE curves [7] (Δ_{MOKE}), also shown for comparison in table 1. Considering that a thickness of Δ Å of pure Co is *homogeneously* diffused in 50 Å of $Gd_{1-x}Co_x$ alloy (which is the fixed thickness of the alloy in all samples), one can easily calculate the final concentration that the alloy would reach, taking into account the different structures and volumes per atom. This calculation yields a Co percentage of 52 for the *pure* series, 59 for the *eutectic*, and obviously 60 for $x = 0.60$, since there is no evidence of interdiffusion in this case. The *pure* series, as we have discussed above, is very likely to be the most inhomogeneous. In fact, remains of nanocrystalline Gd grains appear in XRD scans up to $t = 35$ Å (not shown). This explains the lower value found for its calculated percentage, also in agreement with the lower value found for the magnetization of the Co layers once formed (table 1), measured as the slope of the linear region. This is in agreement with a recent theoretical study which indicates a preferred alloy composition in this system of $Gd_{0.46}Co_{0.54}$ [11].

4. Conclusions

It is well known that good quality Gd/Co multilayers are difficult to obtain due to the strong interdiffusion between layers that takes place in this system. This limits the potential applications of this artificial ferrimagnetic system. We have shown in this work that it is possible to obstruct interdiffusion in a Gd/Co-like system substantially by using an amorphous $Gd_{1-x}Co_x$ alloy instead of pure crystalline Gd. This allows us to obtain well structured multilayers even for thicknesses on the nanometre scale. Several series with different Co contents (x) have been tested, and the results show that interdiffusion in these series of multilayered structures occurs on increasing the Co content of the alloy up to around 60% Co. Once this alloy composition has been reached, a well structured multilayer is formed. In the $x = 0.60$ series, interdiffusion is almost completely avoided, while the magnetic structure is conserved, which opens up a new field of applied and fundamental research into these *giant* ferrimagnetic systems [12].

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