Stuctural And Magnetic Characterization Of Co_xZn_{1-x}/Cu Multilayers Obtained by Electrodeposition

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We present the experimental results of $(Co_xZn_{1-x}/Cu)_n$ multilayers (3<x<10) grown using the electrochemical dual bath method. The X-ray diffraction patterns have shown that the CoZn structural lattice parameters are close to those of the monoclinic $CoZn_{13}$ compound.
We have developed an analytical model in the X-ray kinematical theory adapted to the electrodeposited (Co_xZn_{1-x}/Cu) multilayers. We have shown that the model can give interesting structural information about the multilayer components, and reproduces the position of the satellite peaks around the main diffraction peak . Thus we have deduced the multilayer period and performed comparison between experimental results and the analytical model.
The magnetic properties at room temperature reveal both superparamagnetic and ferromagnetic features. The inclusion of Zn into the magnetic layer and the existence of CoZnCu based alloy at the interfacial regions explain the magnetic properties. The magnetoresistance (MR) loop displays a broad , rounded maximum and the saturation is not observed even at high applied fields. The MR(H) behaviour and its small ratio can be attributed to interfacial effects .
Keywords : $(Co_xZn_{1-x}/Cu)_n$; multilayers; electrodeposition; magnetoresistance; superparamagnetism;

I. INTRODUCTION

Since the discovery of giant magnetoresistance in Fe/Cr superlattice with antiferromagnetic coupling between adjacent layers [1], several preparation techniques like molecular beam epitaxy (MBE), evaporation, sputtering… have been used to grow metallic multilayers. Electrochemical deposition technique for multilayer alloyed system of transition metal has not been extensively investigated even if certain properties offered by this technique can be comparable to those of the others techniques [2]. It has been shown in previous studies that the magnetoresistance of electrodeposited Co/Cu multilayers is comparable to the sputtered and MBE grown Co/Cu samples and a small antiferromagnetic coupling between magnetic layers gives rise to relatively high magnetoresistance [3].
The CoZn alloy presents, in general, two main crystalline phases: $CoZn_{13}$ (monoclinic) and Co_5Zn_{21} (cubic) and their well known structural parameters. Recently a new CoZn phase has been determined and corresponds to the Co_2Zn_{13} alloy with a complex structure that is described as built from icosahedra [4].
Our aim in this work was to produce electrodeposited $(Co_xZn_{1-x}/Cu)_n$ multilayers not studied up till now and to clarify the structural, magnetic and transport properties , in particular to explain the correlation between the magneto-transport properties and the microstructure. The calculation of the structural factor characterizing the atomic distribution and then the determination of some structural parameters as modulation period, were performed using an approach from the X-ray kinematical theory adapted to our specific multilayers.

II. EXPERIMENTAL DETAILS

The (Co_xZn_{1-x}/Cu) multilayers have been grown using the electrodeposition technique by the dual bath. The magnetic Co_xZn_{1-x} layer was deposited in the electrolyte bath containing $CoCl_2,6H_2O$; $CoSO_4,7H2O$; $ZnSO_4,7H_2O$; $(NH_4)_2SO_4$ and H_3BO_3. The Cu layer was deposited during t =2s for a fixed current density of about 20mA/cm^2 in the electrolyte bath which contains $CuSO_4,5H_2O$ and H_2SO_4 .
The electrolyte for the electrodeposition of Co_xZn_{1-x} layer is a modification of one that has been used for the thin films by I. Kirilova and all [5]. The thickness of CoZn was varied by using different currents and different deposited times whereas the Cu layers thickness was always constant (t_{cu} = 30 Å).
The electrodeposition of multilayers is carried out in a standard three electrode electrochemical cell at room temperature. The samples have been

deposited on glass (or SiO_2) substrates, covered by a 2400 Å thick Cu buffer layer sputter-deposited at room temperature. Scanning electron microscopy (SEM) observation shows homogenous surface morphology. The atomic percentages of the deposit elements were found by the energy dispersive X-ray analysis (EDAX). Several techniques as high angle X-ray diffraction, alternating gradient force magnetometer (AGFM) and four-terminal magnetoresistivity measurements have been used to characterise these samples. The X-ray diffraction and the analysis of electrochemical deposit parameters permitted to deduce the layers thicknesses mentioned in this paper. The magnetization and MR loops were measured with the field in the plane under a maximum field of 14 kOe at room temperature. The ferromagnetic resonance (FMR) spectra at 9,8GHz were obtained as function of the magnetic field applied parallel and perpendicular to the plane.

III. RESULTS AND DISCUSSION

We have investigated the structural characteristics of the $(Co_{3,8}Zn_{96,2}$ / $Cu)_{15}$, $(Co_{4,6}Zn_{95,4}$ / $Cu)_{10}$, $(Co_{9,7}Zn_{90,3}$ / $Cu)_{20}$ electrodeposited multilayers by X-ray θ-2θ diffraction using $CoK\alpha_1$ radiation (λ_{Co} =1,789 Å). The **fig1-a** shows the $(Co_{3,8}Zn_{96,2}$ / $Cu)_{15}$ X-ray pattern . Apart from the strong (111) and (200) Cu buffer diffraction peaks we observe only a small peak at 2θ = 42,65° i.e. near the ($\bar{4}02$) $CoZn_{13}$ Bragg peak . For this sample the magnetic CoZn layer thickness is small ($t_{Co3,8Zn90,3}$ = 10 Å) and then the interdiffusion at the CoZn-Cu interface is sufficient to destroy the coherence allowing to the emergence of a well-defined structure .

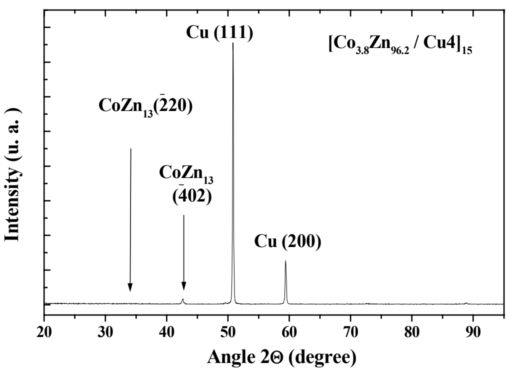

Fig1-a: θ-2θ spectrum recorded for the $(Co_{3,8}Zn_{96,2}$ / $Cu)_{15}$ multilayer

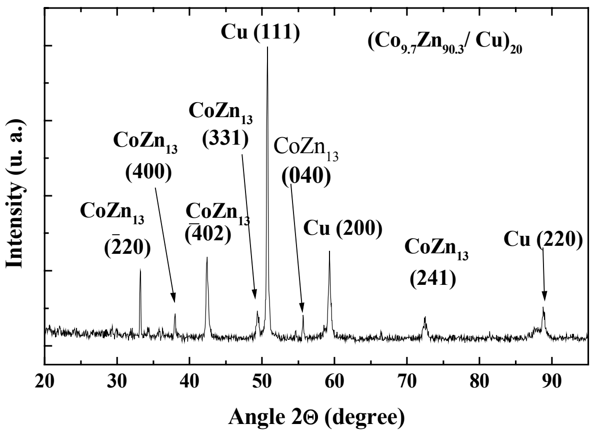

Fig1-b: θ-2θ spectrum recorded for the $(Co_{9,7}Zn_{90,3}Cu)_{20}$ multilayer

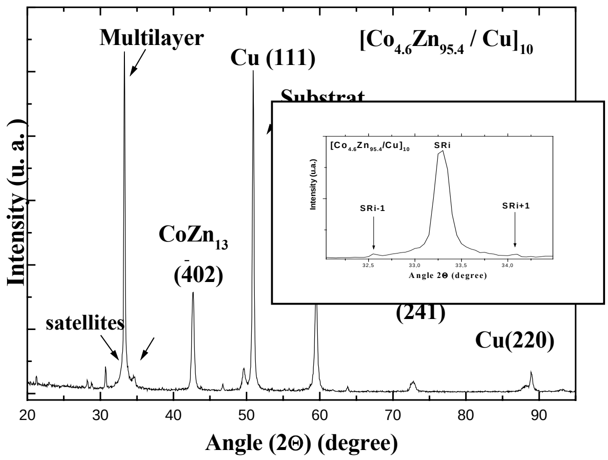

Fig.1-c: θ-2θ spectrum recorded for the $Co_{4,6}Zn_{95,4}$ / $Cu)_{20}$ multilayer.

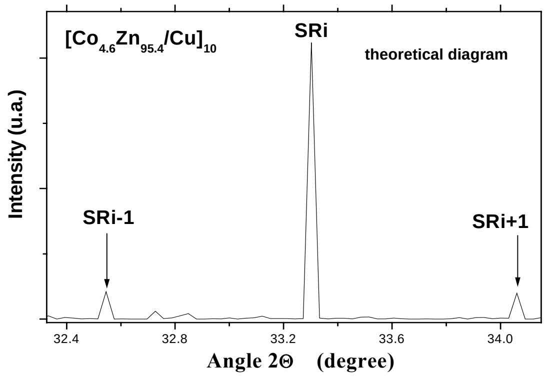

Fig 2-a : Theoretical diagram θ-2θ spectrum for the $(Co_{4,6}Zn_{95,4}$ / $Cu)_{20}$ multilayer.

For the $(Co_{9,7}Zn_{90,3} / Cu)_{20}$ multilayer which magnetic thickness is ($t_{Co9,7Zn90,3}$ = 120 Å) the scratched X-ray diffraction pattern with several identified peaks (fig.1-b) confirms the presence of only $CoZn_{13}$ phase in the bulk of magnetic layer without any preferential direction. The determination of the structural parameters for this phase indicates that its lattice is no constrained and then not affected by the multilayer modulation.

Otherwise for the $(Co_{4,6}Zn_{95,4} / Cu)_{10}$ multilayer with intermediary Co concentration, the spectrum (fig1-c) exhibits a significant intensity near the ($\bar{2}20$) and ($\bar{4}02$) monoclinic $CoZn_{13}$ Bragg peaks positions at respectively 2θ = 33,30° and 2θ = 42,65°. Around the first main peak labelled SR_i, we observe two weak SR_{i-1} and SR_{i+1} satellite peaks at respectively $2\theta_{i-1}$=32.56º and $2\theta_{i+1}$=34.07 . To be confident that these peaks correspond to the first order superlattice satellites and to determine the superlattice period we propose theoretical model for the simulation of experimental XRD spectrum.

IV. THEORETICAL APPROACH:

In a first approach, we use the model with two crenels [6], containing two layers of Co_xZn_{1-x} and Cu, and made up of N periods. The structural factor F(q) which characterizes its atomic distribution, is written:

$$F(q) = f_{Cu} \sin(qn_{Cu}d_{Cu}/2)/\sin(qd_{Cu}/2) + f_{CoZn} \exp(iq\Lambda/2) \sin(qn_{CoZn}d_{CoZn}/2)/\sin(qd_{CoZn}/2) \quad (1)$$

with:

f_{Cu} and f_{CoZn} being respectively the scattering factors of the Cu and CoZn atoms;

d_{Cu} and d_{CoZn} are the reticular distances of the species constituting multilayer for a determined orientation;

n_{Cu} and n_{CoZn} the numbers of reticular planes associated to Cu and CoZn;

q the scattering vector ($q = 4\pi \sin\theta/ \lambda_{Co}$);

$\Lambda = n_{Cu}d_{Cu} + n_{CoZn}d_{CoZn}$ the superperiod of the multilayer.

The atomic scattering factor for a determined atom is expressed as [7] :

$$f = 3Z/(X)^3 [\sin(X) - X\cos(X)] \quad (2)$$

with $X=4\pi \sin(\theta) R / \lambda_{Co}$, R the radius of the atom and Z its atomic number.

For the calculation of f_{Co}, f_{Zn}, we choose the angular position which corresponds to the position of the main peak at 2θ = 33,30° for $CoZn_{13}$. We obtain f_{Co}=12.9 and f_{Zn}=12.30. For the Cu(111) nonmagnetic layer the atomic scattering factor value is f_{Cu}=5.758.

For the intensity calculation we used the experimental parameters of the $(Co_{4,6}Zn_{95,4} / Cu)_{10}$ electrodeposited multilayer : f_{CoZn}=24.66 ; f_{Cu}=23.03 ; d_{Cu}=2.032 Å; n_{Cu}=15; N=10; x=4,60; $\Lambda_{cal} = n_{Cu}d_{Cu} + n_{CoZn}d_{CoZn}$; d_{CoZn}=3.121 Å; λ_{Co} =1.789Å . To have the main Bragg peak in the same angular position as that of the experimental curve we vary n_{CoZn}, the number of the reticular planes.

The main peak, which appears on the theoretical diagram is surrounded by less intense peaks, which constitute the satellite peaks (fig2-a) with the associated diffraction angles θ_i, θ_{i+1}. This enables us to determine the super-period of the multilayer Λ_{th} from the formula:

$$\Lambda_{th} = \lambda_{Co} /(\sin\theta_{i+1}-\sin\theta_i) \quad (3)$$

with : θ_{i+1}=34.06º and θ_i=32.53 º and then: Λ_{th}=69.92 Å.

We conclude that the satellite peaks SR_{i-1} and SR_{i+1} which appear in the experimental diagram (fig1-c) are the first order satellites of the superlattice peak. The presence of these satellites around the main peak ($\bar{2}20$) indicates the good quality of the sample and allows to evaluate the experimental superperiod Λ_{exp} of the $(Co_{4,6}Zn_{95,4} / Cu)_{10}$ multilayer and consequently the thickness of the magnetic layer. We obtain Λ_{exp} =70.85 Å and $t_{Co4.6Zn95.4}$= 40.85 Å. This result is in agreement with the theoretical result obtained from the X-ray kinematical theory.

V. MAGNETIC PROPERTIES

We have compared in the (fig.3-a) and (fig.3-b) the magnetization loops respectively for the 480 Å $Co_{3,8}Zn_{96,2}$ electrodeposited layer and the $(Co_{3,8}Zn_{96,2} /Cu)_{15}$ multilayer. For the single layer it seems that the saturation is easily reached with respect to the $(Co_{3,8}Zn_{96,2} /Cu)_{15}$ multilayer, where the saturation magnetization is not reached even for applied magnetic field as high as 14 kOe . This behaviour is confirmed for the others multilayers with higher Co concentration (fig.4), which indicates the presence of a superparamagnetic contribution.

The presence of both ferromagnetic and superparamagnetic contributions and their corresponding magnetic feature can be due to the interfacial mixing. The ferromagnetic contribution increases with x at% Co as is evidenced by the coercive field and reduced remanence magnetization values. (see Table)

	H_c (Oe)	M_r / M_0	ΔM_R %
$(Co_{3,8}Zn_{96,2} /Cu)_{15}$	38,4	0,06	0,23
$(Co_{4,6}Zn_{95,4} / Cu)_{10}$	39,7	0,11	0,25
$(Co_{9,7}Zn_{90,3} / Cu)_{20}$	45,8	0,13	0,26

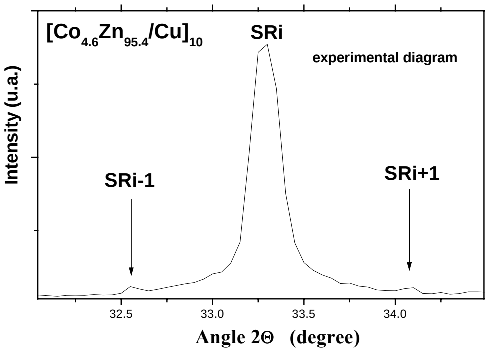

Fig 2-b: θ-2θ spectrum recorded for the $(Co_{4,6}Zn_{95,4}/Cu)_{20}$ multilayer around the main peak.

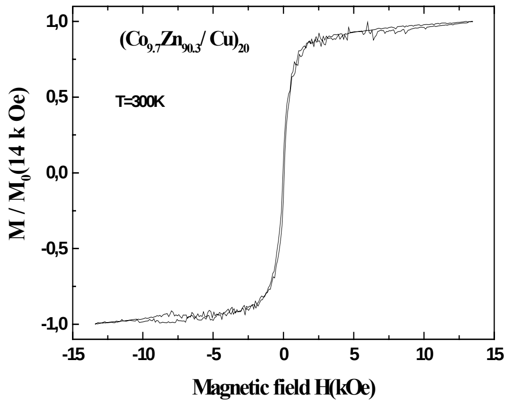

Fig 4 : Magnetization loop for the $(Co_{4,6}Zn_{95,4}/Cu)_{20}$ multilayer with the magnetic field in the film plane.

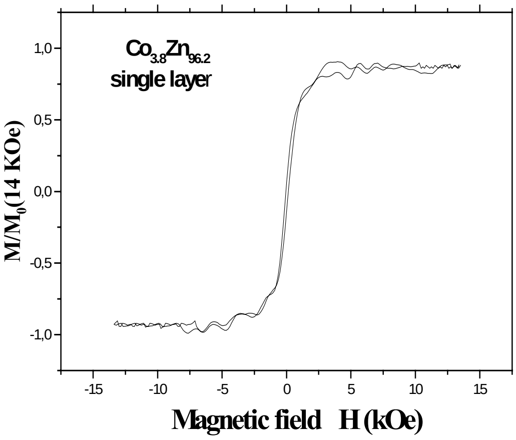

Fig 3-a : M(H) for the electrodeposited $Co_{3,8}Zn_{96,2}$ film.

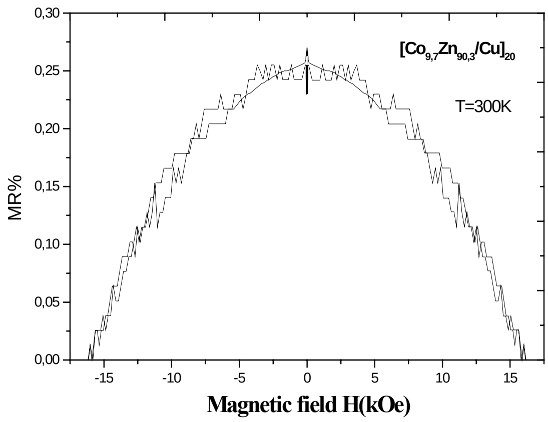

Fig 5: Magnetoresistance loop for the $(Co_{9,7}Zn_{90,3}/Cu)_{20}$ multilayer with the magnetic field in the film plane.

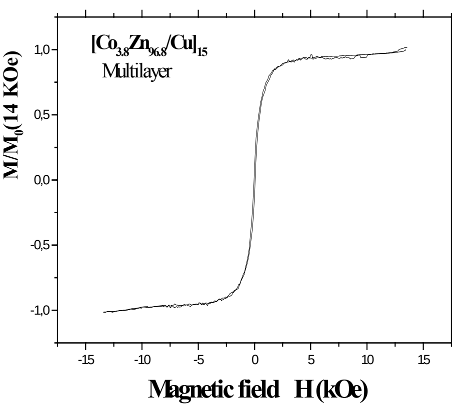

Fig 3-b : M(H) for the electrodeposited $Co_{3,8}Zn_{96,2}$ multilayer.

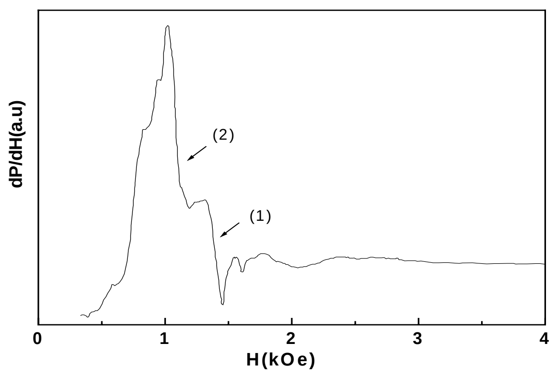

Fig 6 : FMR spectrum for $(Co_{4,6}Zn_{95,4}/Cu)_{20}$ multilayer for parallel ($H_{\parallel}$) applied field at 300K.

VI.MAGNETORESISTIVE PROPERTIES

The magnetoresistance measurements were performed at room temperature with the magnetic field reaching 14kOe in the film plane. Figure 5 shows the magnetoresistance curve as function of the magnetic field for one of the studied electrodeposited multilayers $(Co_xZn_{1-x} / Cu)_n$. The MR displays a broad, rounded maximum at H = 0 and does not present saturation even for the highest applied field. We note also that the MR ratios obtained for different samples are relatively small compared with other systems prepared by the same deposition technique like: Co/Cu [3]; CoZr/Cu [8]; and CoCu/Cu [9]. In addition, the MR ratio aren't sensitive neither to the Co concentrations nor to the magnetic layer thickness. The small MR maximum values can be explained by several effects: (i)a shunting effect due to the thick Cu buffer layer; (ii) the influence of the Cu interlayer thickness on the transport and diffusion process. It is proved that a relatively thick Cu interlayer reduces the flux of polarised electrons transmitted from one ferromagnetic layer to the other [10]; (iii) the existence of a large mixing at the interfaces giving rise to a ternary CoZnCu phase. In this phase, the influence of Cu is to increase magnetic isolation of magnetic particles and then can be responsible to both attenuation of transport process and superparamagnetism that is at the origin of a rounded magnetoresistance behaviour. Such a ternary CoZrCu alloy at the interfaces was already observed in sputtered CoZr/Cu/Co sandwiches [8]. It was shown that this disordered phase affects both the mean-free path for electrons across the CoZr/Cu interface and the spin dependent scattering asymmetry coefficient and then lowers strongly the magnetoresistance rate.

VII. FMR MEASUREMENTS

Ferromagnetic resonance was observed at 300 K and 9.8 GHz with the field applied parallel ($H_{||}$) to the specimen plane. The spectrum of the $(Co_{4,6}Zn_{95,4} / Cu)_{10}$ multilayer reported in figure 6 presents an intense mode and additional other modes with smaller intensities. This is characteristic of inhomogeneous sample, which is in agreement with the magneto-transport results.

VIII. CONCLUSION

We have shown that it is possible to grow well defined electrodeposited multilayers consisting of ferromagnetic Co_xZn_{1-x} alloys separated by non magnetic Cu layer. We have identified the main phase and determined the structural parameters using the X-ray kinematical theory. With the interfacial phenomena we have explained the superparamagnetic magnetization behaviour and the small magnetoresistance as compared to Co/Cu prepared by the same technique. From the FMR measurements we have shown the inhomogeneous character of the films.

Acknowledgements

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