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Compositionally modulated magnetic films

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1. Introduction

Superstructured metallic superlattices constitute a new class of materials which are not found in nature (Falco and Schuller 1984). Hence one could expect to find in them new properties which could cover a wide range of fields such as structures, superconductivity and magnetism, to name only a few. Superlattice semiconductors GaAs-GaAlAs are known for over a decade and are already used in practical applications. However, magnetic superlattices have attracted the attention of some laboratories only recently (Young *et al* 1977; Gyorgy *et al* 1980). These materials, also known as compositionally modulated films (CMF), consist of thin films of two metals deposited in an alternate sequence onto an appropriate substrate. They enable us to study several interesting aspects in magnetism. One can enumerate a few as follows: the thickness dependence of the magnetization, the effect of the proximity on the ferromagnetism of a layer, the interface magnetism and so on. Of course, in order to study the above aspects appropriate measuring techniques have to be used. The most common are magnetization measurements, ferromagnetic resonance (FMR), Mössbauer spectrometry and polarized neutron diffraction (Shinjo *et al* 1983; Walker *et al* 1984). Though ideas regarding magnetic couplings in such sandwiches have been there for a very long time, experimental work was impeded for want of suitable samples. The remarkable progress in the thin film technology that we have witnessed in recent years and the powerful techniques of film characterization have now enabled us to obtain suitable samples for carrying out the above mentioned studies. While superlattice semiconductors are obtained with great perfection, though using rather a very expensive technique such as molecular beam epitaxy, it is possible to utilize less sophisticated techniques for obtaining magnetic CMF.

Magnetic CMF can be divided into three categories: (1) epitaxially deposited superlattices e.g. Ni/Cu; (2) multilayers of polycrystalline metals e.g. Co/Nb; (3) multilayers of amorphous films e.g. Fe-Si/Si. In the first category, the lattice constant remains the same along the thickness but only composition and magnetic properties are modulated. Properties of Ni/Cu (Zheng *et al* 1982) and Fe/(Pd, Sb, V) (Shinjo *et al* 1983) have been reported. Detailed studies have been made on Ni/Cu (Gyorgy *et al* 1982). It has been found that both the magnetic moment and the Curie temperature T_c of Ni in Ni/Cu are reduced with respect to the bulk value. The Fe multilayers have been studied by Shinjo and his collaborators (Shinjo *et al* 1983) using Mössbauer spectroscopy. For Fe thickness below 1·5 nm the spectra depend sensitively on Fe thickness. A distribution in the hyperfine field was obtained. A difference in the magnetic properties of the top Fe layer and the one near substrate has been observed.

One can say that the fascinating field is just opening up and as is to be expected more and more laboratories are getting interested in it. Work in our laboratory started in 1983.

In this paper we will describe our work on two typical systems Co/Nb and Co/Mn (Krishnan and Janz 1984; Sakakima *et al* 1985), where Nb is non-magnetic and Mn is antiferromagnetic. Thus a comparative study is informative as regards magnetic coupling. Furthermore Mn is an excellent candidate for spin echo studies. The films were characterized using x-rays and Secondary ion mass spectroscopy (SIMS). We carried out magnetization measurements, FMR and spin echo studies in the temperature range 4·2 to 290 K. Finally we mention some results on Brillouin light scattering studies which are particularly interesting for studying some collective excitations in these layered structures.

2. Experimental methods

The CMF can be prepared by either sputtering or evaporation. Each technique has its own advantages. In our laboratory the samples are prepared by evaporation. Indeed it is felt that sputtering could induce some mixing at the interface due to relatively higher energy of the atoms arriving at the substrate.

The CMF reported here have been evaporated in an alternate sequence using two *E*-beams fitted in a Ultra high vacuum (UHV) chamber. Ti ion pump and Ti sublimation produce the vacuum in our system, which is 1×10^{-10} Torr to start with and $3\text{–}6 \cdot 10^{-9}$ Torr during film deposition. Both glass and Si substrates have been used which were maintained close to 20°C by water cooling. The evaporation rate, generally in the range 0·05 to 0·2 nm s^{-1}, and the thickness are controlled using a quartz oscillator and a microprocessor (INFICON). Though the thickness reproducibility is accurate to ± 1 Å the real thickness is calculated by prior calibration and is expected to be accurate only to ± 10 %. Generally, the cobalt layer is on the top of the stack. The sublayer thickness was varied from 1 to 50 nm and as many as 60 bilayers were deposited in some cases.

The modulation was verified in some cases by small angle x-ray scattering. The depth profiling was carried out by SIMS but the resolution was insufficient for analysing the interface purity.

A vibrating sample magnetometer (VSM) and a Faraday balance were used for measuring the magnetization. FMR was observed in the x-band, with the d.c. magnetic field applied in the film plane ($H_{||}$) and normal to it ($H\perp$). We obtain the effective magnetization $4\pi M' = 4\pi M\text{-}H_A$, where H_A is the anisotropy field. Spin echo spectra were taken at 4·2 K, either with or without an external field.

Brillouin light scattering experiments were carried out at the Fraunhofer Institut für Angewandte-festkorperphysik, Freiburg. One obtains the effective magnetization and the g factor as in FMR besides some information about the thicknesses of the sublayers with the help of theories developed recently to calculate magnon energies in CFM. (Camley *et al* 1983; Grünberg and Mika 1983).

3. Experimental results and discussions

3.1 *X-ray diffraction*

In small angle diffraction the artificial periodicity due to alternate layers of the two metals could be observed. Our study of Co/Mn revealed the first and second order reflections indicating negligible interdiffusion of Co and Mn (Sakakima *et al* 1985). Nevertheless spin echo measurements indicated the contrary as we shall describe later which simply means that in certain cases magnetic studies could be more powerful. From these x-ray reflections the period was calculated which agreed with the value determined from the thickness monitor. Due to want of enough number of bilayers such a study could not be carried out on Co/Nb samples.

3.2 SIMS

Considering the resolution limit of the apparatus which is expected to be about 1·5 nm, we examined a few samples where the sublayer thickness was greater than 5 nm. Figure 1 shows a typical result for a Co/Nb sample where the Co counts are recorded as a function of etching time, which instead of being of rectangular wave form shows broad peaks. This is precisely due to lack of resolution. We shall see that other magnetic measurements yield more information on the state of the interface. It was also found that the oxygen content was negligibly small.

3.3 *Magnetization*

VSM measurements were carried out only at 290 K. Figure 2 shows the decrease in the magnetization in Co/Mn CMF as a function of t_{Co}. Also are indicated by dotted lines the trend considering either one or two dead layers of cobalt. The experimental data lie between the two lines. The decrease in the magnetization with thickness of the magnetic sublayer is a typical result in CMF. In the Co/Nb system, however, the magnetization decreases faster and for $t_{Co} = 5$ nm it has fallen by about 18% and disappears for $t_{Co} < 2$ nm (Krishnan 1985). Table 1 shows the results, where data on a single layer Co films of about 85 nm thick is also recorded. However for $t_{Co} > 10$ nm the magnetization

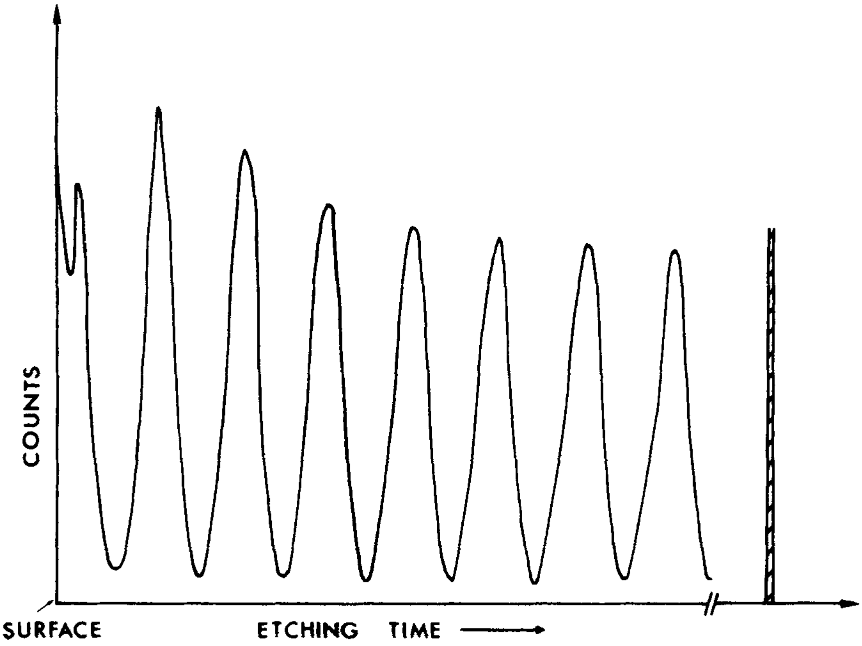

Figure 1. SIMS profile of Co concentration in sample 3.

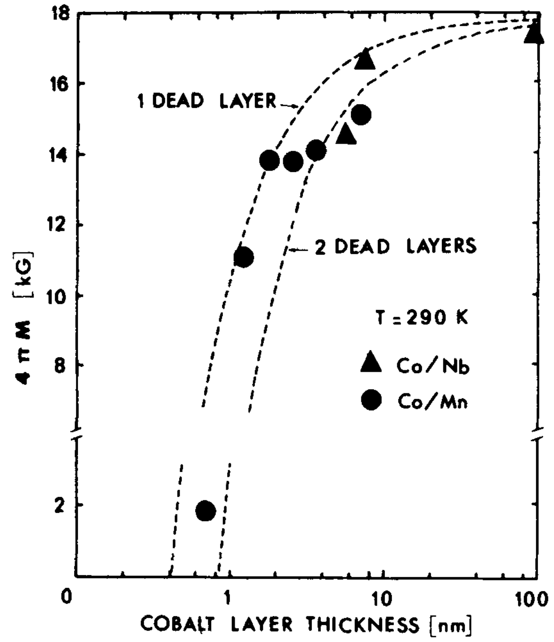

Figure 2. The thickness dependence of magnetization in Co-Nb and Co-Mn CMF samples.

Table 1. Growth parameters of CMF and magnetization at 290 K

Sample	Sub-layer thickness nm ± 10% t_{Co}	t_{Nb}	N° of bilayers	$4\pi M$ kG 10%
1	1·4	1·8	2·1	non magnetic
2	5·0	1·8	8	14·0
3	7·0	2·3	10	17·0
4	7·0	9·0	10	16·8
5	10·5	9·0	11	17·0
6	21·0	4·5	5	17·0
7	85	single layer		17·0

attains the bulk value independent of t_{Nb} in the range studied here. It should be mentioned here that these measurements are global and give an average value. Faraday balance measurements were done on a couple of samples only to obtain the temperature dependence of the magnetization and will be discussed in the following section.

3.3a *FMR at* 290 *K*: FMR turns out to be a more potential tool for studying these CMF samples and more information is obtained. As mentioned earlier, from the $H_{\parallel}$ and $H_{\perp}$ values, the g factor and the effective magnetization $4\pi M'$ were calculated. Knowing $4\pi M$ from VSM measurements one can thus calculate the uniaxial anisotropy field, H_A.

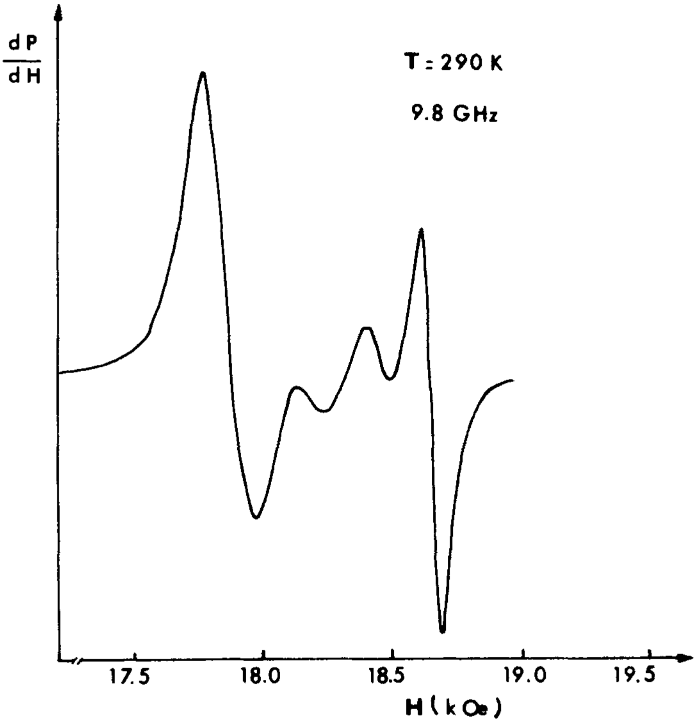

Figure 3. FMR spectrum for the perpendicular configuration for sample 3.

The perpendicular resonance spectra in general show more than one absorption mode (Krishnan 1985). For sample 1, in the Co/Nb system one strong mode is observed followed by two more whose intensity is about 2 % of the first one. In other samples one could observe at least five modes of comparable intensity. Figure 3 shows the spectrum for sample 3. The line widths are on the order of 60 Oe which are indeed narrow. The presence of several absorptions could be considered as those arising from regions of varying magnetization or, in other words, due to interdiffusion of Co and Nb. In order to check this a few samples were annealed in UHV at 240°C for about 4 hr in order to induce some interdiffusion. However $H_{\perp}$ spectra remained essentially the same with small shifts in the position of two modes in the low field side. This led us to conclude that interdiffusion was negligible even at 240°C. This fact along with the rather sharp lines observed would in our opinion indicate that interdiffusion is negligible in these Co/Nb films. Angular dependences of H_{res} was studied but could not give any clear result as to whether the different modes arise from regions of different magnetization. However in the case Co/Mn samples for $t_{\mathrm{Co}} < 30$ Å on the contrary one could get some indication that there were regions of varying magnetization. A similar result has been reported on sputtered Ni/Mo CMF (Pechan *et al* 1985). FMR measurements thus go a step further than those by VSM, probing somewhat locally the layered structure. At this stage of work the multiple resonance observed is attributed to the multilayered structure.

The highest $H_{\perp}$ mode was considered for the calculation of $4\pi M'$ and g and the results for Co/Nb are given in table 2 where the anisotropy field, H_A value, is also included. It is seen that a small uniaxial anisotropy is present and it goes through a

Table 2. Some FMR properties at 290 K and the spin-wave stiffness constant D

Sample	$4\pi M'$ kG ± 1%	$4\pi M$-$4\pi M'$ = H_A kOe ± 20%	Linewidth Oe ΔH	Linewidth Oe ΔH	g	D meV·A^2 ± 10%
2	12·9	1·1	55	70	2·106	300
3	14·4	2·6	70	100	2·024	
4	14·3	2·7	80		2·080	
5	15·5	1·5	90	120	2·130	280
6	16·5	0·5	40	100	2·120	
7	17·3	0	40	180–240	2·120	390

maximum value of 2·6 kOe for $t_{\text{Co}} = 7$ nm. The absence of such an anisotropy in single layer Co films confirms that this anisotropy does not arise from magnetoelastic effects and has to do with the multi-layered structure. The g factor in all the samples is close to 2·1 which agrees with the well known value of 2·17 for cobalt. Similar results are obtained also for Co/Mn samples. The fairly low line width (40 Oe) observed on single layer Co film lead us to expect a f.c.c. structure for this film. Also the coercive field in this sample was less than 10 Oe.

3.3b *FMR at low temperatures*: Both $H_\perp$ and $H_{||}$ were studied as a function of temperature in the range 4·2 K to 290 K. The results for Co/Nb are totally different from those for Co/Mn particularly for $t_{\text{Co}} < 3$ nm. Let us first consider the Co/Nb system. For samples with $H_\perp$ spectra containing numerous modes not all of them could be observed in the low temperature range because some of them coalesce into one broad band. However, where the individual modes could be observed down to 4·2 K, $4\pi M'$ was calculated and its temperature dependence was found to follow Bloch's law namely $4\pi M'(T) = 4\pi M'(o)\,|1 - BT^{3/2}|$ neglecting higher powers of T. This law is generally valid for magnetization $4\pi M$ but in our case $4\pi M'$ is considered. This indicates that H_A also follows Bloch's law. We have verified this also for amorphous Co-Au films (Krishnan *et al* 1985a). We also checked the validity of Bloch's law for $4\pi M$ by carrying out measurements on a Faraday balance. Bloch's law was also found to be valid for single layer Co film as is to be expected. Indeed similar results have been found for several amorphous alloys, both metal-metalloid and metal-metal types. One interesting result is that the slope B for CMF is almost twice as high as that in Co films indicating a lowering of T_c for CMF ($B = 3\cdot10^{-6}$ and $5\cdot4\cdot10^{-6}$ K$^{-3/2}$ respectively for the Co film and CMF).

From spin wave theories, the spin wave stiffness constant D is related to the coefficient B through the relation

$$B = 0{\cdot}0587\,\frac{g\mu_B}{M(0)}\left(\frac{k_B}{D}\right)^{3/2}$$

where the symbols have their usual meaning. The D values thus obtained are given in table 2. The value of 390 meV·A^2 for the Co film is smaller than 510 meV·A^2 reported in the literature (Wohlfarth 1980).

As regards the Co/Mn system, results are not so straight forward. For instance in samples where $t_{\text{Co}} < 3$ nm, as the temperature is decreased $H_\perp$ increases from the 290 K value as is to be expected but at a certain temperature T_{Cr} it starts decreasing, which indeed is very peculiar behaviour (Sakakima *et al* 1985). This could mean that for $T < T_{Cr}$ either $4\pi M$ is decreasing or H_A is increasing. To elucidate this, measurements were made with a Faraday balance and it was seen that the magnetization actually decreased for $T < T_{Cr}$. This result was not understood initially but later spin echo studies revealed that some interdiffusion of Co and Mn occurs at the interface. This alloy could then explain at least qualitatively the decrease in $4\pi M$ observed which arises from antiferromagnetic interactions caused by Mn. A confirmation of this hypothesis was obtained with samples, where $t_{Co} \sim 7$ nm, in which case no interdiffusion of Co and Mn takes place; thus the temperature dependence of $4\pi M$ becomes normal as in Co/Nb samples.

3.4 *Spin echo studies at* $2 < T < 4{\cdot}2\,K$

While in Co/Nb samples only ^{59}Co spin echo signal could be studied, in the case of Co/Mn samples one has the added advantage of observing the Mn signal also which indeed clarified several points in the course of this study. Spin echo studies (Krishnan *et al* 1985b; Le Dang *et al* 1985) yield three important parameters, namely, the frequency of the nuclear signal, the line shape and finally the signal intensity. For convenience let us discuss first Co/Nb and then Co/Mn systems.

The ^{59}Co signal from the single layer Co film is centered near 222 MHz (figure 4), which is slightly smaller than 228 MHz observed in h.c.p. cobalt but closer to that of f.c.c. cobalt namely 217·5 MHz. This small difference could arise from stacking faults. It is interesting that in our case cubic cobalt is obtained. This confirms our earlier hypothesis deduced from relatively low resonance line widths. The signals from all CMF samples are also centered at about 222 MHz indicating that here also the Co sublayers

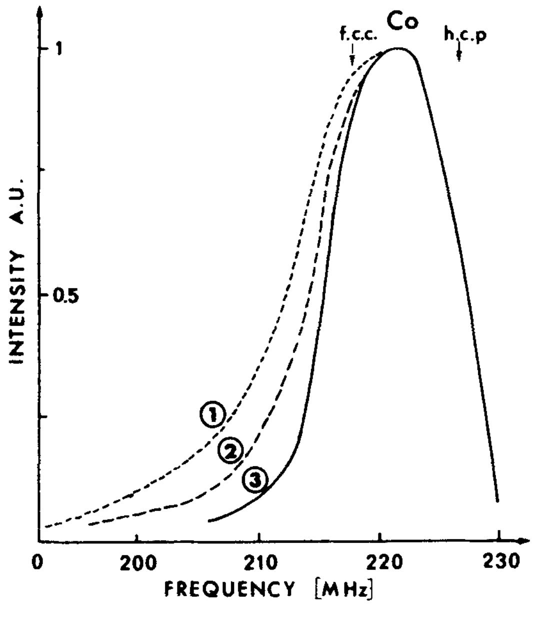

Figure 4. Spin echo spectra for Co single layer (3) and samples 3 (2) and 2 (1).

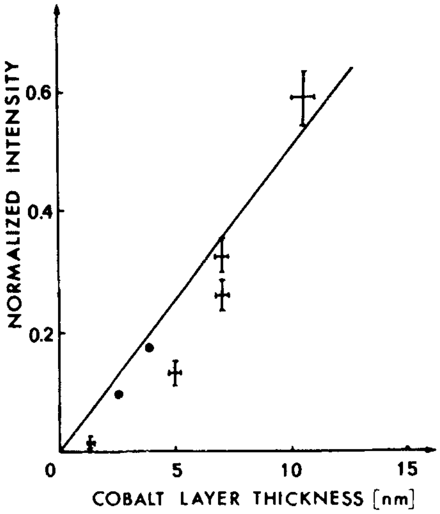

Figure 5. Normalized spin echo signal intensity versus the cobalt layer thickness in Co-Nb CMF samples at 4·2 K.

present a f.c.c. structure. The most important result is that in CMF samples even where t_{Co} = 1·4 nm the frequency is the same which indicates that there are layers of cobalt with the magnetic moment as high as in the bulk. So considering our results from VSM and FMR (where Co magnetic moment decreased for $t_{Co} < 7$ nm) one is led to conclude that this decrease in $4\pi M$ is a global effect and some cobalt atoms do still conserve their bulk moment. The line shape shows that the low frequency tail gets more and more pronounced as t_{Co} is decreased. This would indicate the presence of Co (in the sublayers) with a reduced moment. The study of the intensity of the Co signal from the various samples gives an interesting result. The intensity was normalized to a unit area and divided by the number of Co sublayers. Figure 5 shows the result. The straight line passes through the origin and the intensity point corresponding to the single layer cobalt film (treated as bulk). This point is however not shown in the figure in order that a proper scale could be chosen to bring out the results on CMF. The data points for samples with t_{Co} = 10 and 10·5 nm lie close to the line. However for $t_{Co} < 7$ nm, the experimental points fall below the line indicating the presence of magnetically dead Co layers. For instance in CMF with t_{Co} = 5 nm there are about 5 dead layers. Note that even for t_{Co} = 1·4 nm the intensity is non-zero.

In Co/Mn samples the results are more complex and richer as one could also observe Mn nuclear singals in some cases. For instance, in samples where $t_{Co} >$ 3·6 nm, one observed the usual Co signal centered near 222 MHz similar to Co/Nb samples. But in Co/Mn samples where t_{Co} = 1, 1·8 and 2·5 nm the cobalt spectra are considerably broadened and an extra signal is observed at about 420 MHz which is attributed to Mn atoms. The fact that the Mn signal disappears for $t_{Co} >$ 3·6 nm would indicate that in this case a continuous film is formed. For $t_{Co} <$ 3·6 nm, the film is porous and the Mn atoms getting into these pores acquire a magnetic moment due to cobalt-nearest neighbours. In our case the very high frequency of 422 MHz would correspond to a moment of 3·4 μ_B as compared to 3 μ_B found for Mn in f.c.c. cobalt. This particularly high value for Mn is not well understood at present. The other features include a shoulder observed on the higher frequency side in the Co spectra which would indicate the presence of some Co atoms with exhalted magnetic moment.

3.5 *Brillouin light scattering*

We present here in a very succinct manner our results on Brillouin light scattering studies on Co-Nb CMF samples (Krishnan *et al* 1984; Rupp *et al* 1985).

The multilayered films with different elastic and magnetic properties give rise to new phonon and magnon modes and the periodicity leads to new bands and band gaps at wave vectors near the center of the Brillouin zone. The in-elastic light scattering technique is well suited to study elementary excitations and particularly to investigate surface spin waves in thin films. The experiment was carried out with an argon laser = 514·5 nm and with a 4+2 tandem Fabry Perot spectrometer (Sandercock 1980). The surface spin waves commonly called Damon Escbach modes follow the dispersion relation $(\omega/\gamma)^2 = H(H+4\pi M)+(2\pi M)^2 w$, where the symbols have their usual meaning and $w = 1-\exp(-2kd)$ where d denotes the film thickness. In the case of multilayered structures for certain values of the thicknesses of the bi-layers the spin wave band is broadened and the degeneracy of its branches is more or less removed. In structures with N alternating layers for example one observes N surface spin wave branches under favourable conditions, if not, all of them may not be seen. We were able to achieve this in samples where $t_{\mathrm{Co}} = 21$ nm and $t_{\mathrm{Nb}} = 1{\cdot}8$ nm and with 5 bilayers. We also found a very good agreement with the theoretical predictions. Besides, the values of $4\pi M'$ and g-factor computed from these experiments agreed very well with those obtained from FMR experiments.

In conclusion, CMF of Co/Nb and Co/Mn have been prepared in UHV by evaporation and several magnetic properties studied. A uniaxial anisotropy has been observed. The FMR spectra consist of several absorptions which are thought to be characteristic of CMF. For sublayers of Co which show the bulk moment, the T_c is still reduced with respect to bulk Co. Spin echo studies reveal that whatever the Co sublayer thickness ($t_{\mathrm{Co}} > 1{\cdot}4$ nm) some Co atoms do conserve the bulk moment. In Co/Mn systems, for $t_{\mathrm{Co}} < 3{\cdot}6$ nm, the films are porous and Mn atoms which apparently fall in the pores acquire a magnetic moment. The presence of dead layers is also demonstrated. Finally some results on light scattering studies are also given.

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