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Ferromagnetic Resonance Studies of Ultrathin Co Layers in Co/Ag Multilayers

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A relationship between microstructure and ferromagnetic resonance of Co/Ag multilayers has been studied in as-deposited and annealed multilayers with ultrathin ($d_{Co} < 1$ nm) Co layers. Depending on the nominal thickness of Co Co/Ag multilayers represent a system of fine magnetic particles ($d_{Co} < 0.4$ nm) or discontinuous layered structure (d_{Co}/0.5 nm). FMR data has been interpreted in the framework of a model of interacting fine particles exhibiting superparamagnetic behavior. Changes in the FMR spectra upon annealing have been attributed to the growth of the Co particles and to a transition from the fcc to hcp atomic structure of the highly (111) textured Co particles.

1. Introduction

Co/Ag multilayers with ultrathin Co layers ($d_{Co} < 1$ nm) represent an intermediate state between multilayer and granular structures. Co/Ag multilayers have been extensively investigated due to a fairly high magnetoresistance [1-5]. The magnetoresistance characteristics were found to be strongly affected by the microstructure of such films. Particle size and shape [1], interparticle distances [3] as well as crystallographic structure of Co [2, 4] play an important role for the magnetotransport properties.

Below a nominal thickness of Co (d_{Co}) of about 0.4 nm discontinuous structure transforms to a quasi-two-dimensional network of fine Co particles [1, 6]. NMR [1] investigations confirmed a disk-like shape of Co particles. A percolation threshold between granular and discontinuous layered structure seems not to be sharp and the transition region extends over 0.4~0.5 nm of nominal Co thickness [6]. For a very small nominal Co thickness of about 0.2~0.4 nm Co particles exhibit almost pure superparamagnetic behavior at room temperature [1, 6].

Interparticle distance is not an easily controlled parameter in granular multilayers but even the continuous Co layers ($d_{Co} > 1$ nm) in the Co/Ag multilayers can be relatively easily transformed by annealing into a more separated discontinuous structure which is favorable from the point of view of the magnetoresistance characteristics [1, 3, 5].

Whether the Co particles in the Co/Ag multilayers have a hcp or fcc atomic structure is not clear. Kingetsu [7] reported a hcp structure in the Co/Ag multilayers deposited by MBE above 323 K. Detailed TEM studies [8] revealed differences between the Co-Ag samples prepared at room temperature and those prepared at high temperature. At low temperatures Co showed a (111) fcc structure and the presence of small clusters of Co in a hcp structure. In contrast the high temperature samples displayed segregated phases of fcc Ag and hcp Co. On the other hand, EXAFS and X-ray diffraction measurements [3] suggested the fcc structure. Also in Co/Mn multilayers [9] a transition from a (111) fcc to a (0001) hcp Co structure has been observed from a sharp increase of the uniaxial magnetocrystalline anisotropy from nearly zero to 2×10^6 erg/cm^3. Most probably, the actual atomic Co structure in the as-deposited Co/Ag multilayers is mixed fcc/hcp with stacking faults [1].

Ferromagnetic resonance (FMR) has been already proven as a good tool to investigate microstructural characteristics of the granular films [10-13]. This paper is mainly concentrated on the relation between microstructure of the Co particles and the behavior of FMR spectra below and above the percolation threshold where the microstructure of nominally ultrathin Co layers is expected to vary from granular (with a superparamagnetic behavior) to a more dense, discontinuous structure. We will be also interested in the changes of FMR behavior upon annealing accompanied with modifications of the microstructure of the ultrathin (discontinuous) Co layers or particles.

2. Experimental Procedures

Co/Ag multilayers were prepared by rf sputtering on Si (111) or glass substrates with a variable Co thickness $0.2 < d_{Co} < 1.0$ nm and a constant Ag thickness $d_{Ag} = 2$ nm. The number of repetitions was kept between 40 and 100. Structural characterization was performed with the high- and low-angle X-ray diffraction (Cu-Kα) as well as with the X-ray fluorescence. X-ray diffraction confirmed the superlattice modulation with a strong (111) texture. The full width at half maximum varied from 1° to 2° for $d_{Co} = 0.4$-0.8 nm, respectively. Magnetization measurements were done at a temperature range from 20~300 K with a Faraday balance in fields up to 5 T. FMR spectra were taken with an X-band spectrometer (9.4 GHz) at the in plane and perpendicular to the plane geometries at room temperature in fields up to 1.2 T. The effective magnetization $4\pi M_{eff}$ was determined from the resonance fields $H_r^{\parallel}$ and $H_r^{\perp}$ using the standard relations (see, for example, [9])

$$\left(\frac{\omega}{\gamma}\right)^2 = H_r^{\parallel}(H_r^{\parallel} + 4\pi M_{eff}) \qquad (1)$$

for the in-plane configuration and

$$\frac{\omega}{\gamma} = H_r^{\perp} - 4\pi M_{eff} \qquad (2)$$

for the perpendicular configuration, where γ is the electron gyromagnetic ratio, ω is the resonance frequency and $4\pi M_{eff}=4\pi\tilde{M} + 2K_U/M$ is the effective magnetization with the first term describing the microstructure dependent demagnetizing field and the second term describing the uniaxial magnetocrystalline anisotropy of a textured granular film with a crystallographic structure of (111) fcc or (0001) Co. The fourth-order anisotropy term was neglected for simplicity.

3. Results and Discussion

The magnetic properties of our multilayers with the ultrathin Co layers were very similar to those already reported in the literature [1]. A granular microstructure of ultrathin Co layers was confirmed with static magnetization measurements. Fig. 1 shows, as an example, the magnetic moment as a function of the applied field divided by the temperature H/T for a Co/Ag multilayer with $d_{Co} = 0.15$ nm. All the data for magnetic moment measured at a wide temperature range from 50 K to 300 K lies on one universal curve described by the Langevin function.

$$M/M_s = L(mH/k_BT). \qquad (3)$$

Fitting the experimental results yields the number N of Co atoms per average cluster $m = N\mu_{Co}$ assuming $\mu_{Co} = \mu_{Co}^{bulk}$. The average particle size determined in such a way for the Co/Ag multilayers with d_{Co} from 0.15 nm to 0.6 nm is plotted in Fig. 2. The most characteristic feature seen in Fig. 2 is that the Co particle size fairly weakly depends on d_{Co} for the nominal Co thickness less than 0.4 nm. A similar behavior has been observed by van Alphen and de Jonge [1] who concluded from NMR data that only the number of three-dimensional islands increases, without appreciable change in shape or size. For $d_{Co} > 0.4$ nm, the particle size sharply increases and the low-temperature magnetic moment plotted versus H/T no longer follows the universal behavior described by Langevin function showing non-zero remanence below T < 100~200 K for multilayers with $d_{Co} = 0.5$~0.6 nm, respectively. Such a behavior reflects the fact that for $d_{Co} > 0.4$ nm Co/Ag multilayers represent a discontinuous layered structure of fairly large Co islands mixed with fine Co particles.

Having the microstructure of our Co/Ag multilayers fairly well characterized, let us discuss its implication in ferromagnetic resonance. Fig. 3 shows the evolution of FMR spectra taken with the external magnetic field applied parallel or perpendicular to the film plane on increasing d_{Co}. A systematic increase of splitting of the resonance line positions for both field orientations is seen. As it is shown in Fig. 4, such a behavior is interpreted in terms of Eqs. (1) and (2) as a consequence of a monotonic increase in the effective demagnetizing field (the effective magnetization) $4\pi M_{eff}$ due to increasing role of interparticle dipolar interactions and/or the uniaxial anisotropy. The lack of the drastic changes in $4\pi M_{eff}$ at $d_{Co} = 0.4$ nm reflect the fact that the effective magnetization depends not only on the size of Co

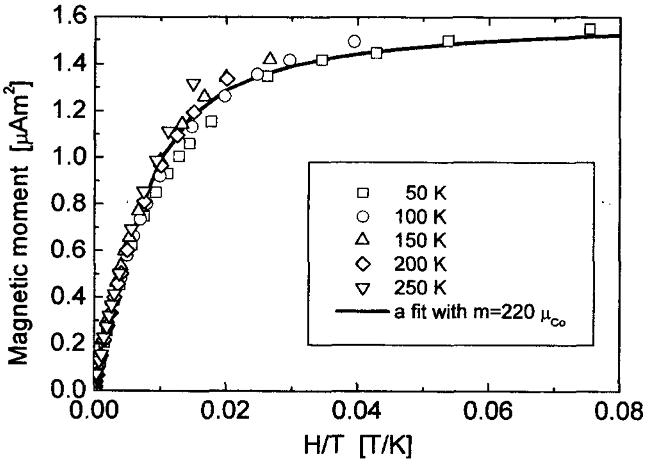

Fig. 1. Magnetic moment as a function of the magnetic field divided by the temperature for the sample 100 {0.15 nm Co/2 nm Ag}. Solid line represents a fit according to Eq. (1) with $m = 220\mu_{Co}$.

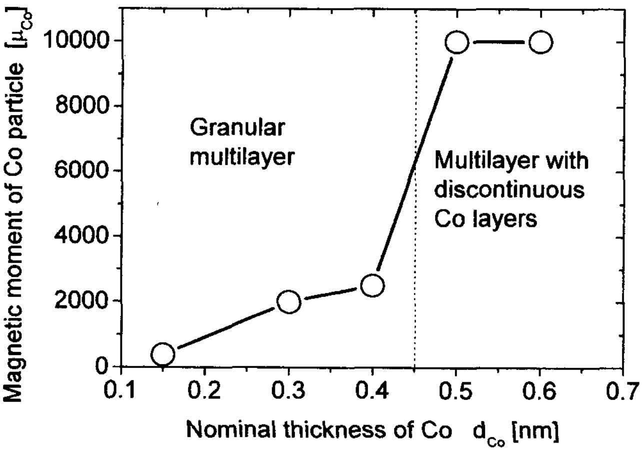

Fig. 2. Average size of a Co particle as a function of the nominal thickness d_{Co}.

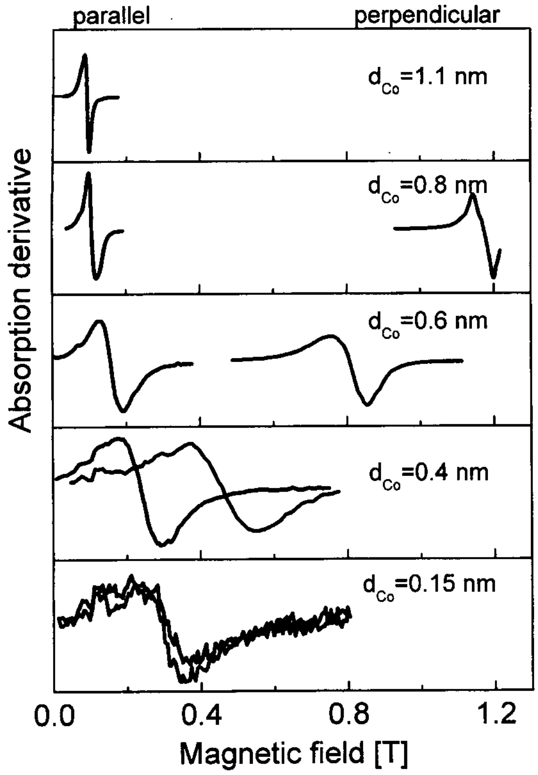

Fig. 3. FMR spectra taken at the parallel and perpendicular configurations of as-deposited {d_{Co} nm Co/2 nm Ag} multilayers.

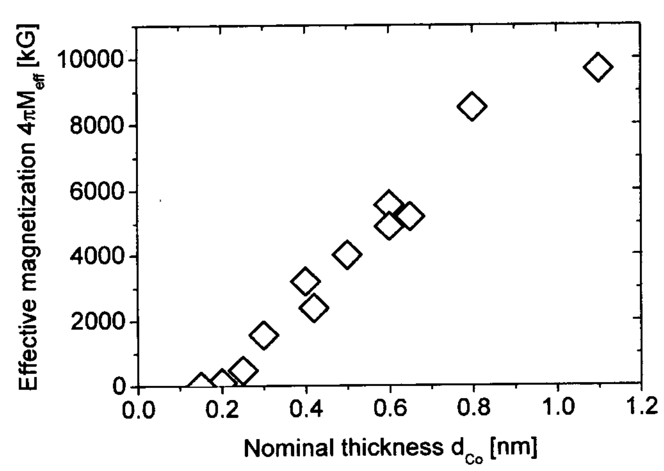

Fig. 4. The effective magnetization $4\pi M_{eff}$ determined from FMR measurements as a function of the nominal thickness d_{Co} for as-deposited Co/Ag multilayers.

particles but also on their volumetric filling factor in a Ag matrix. Additionally, as will be discussed below, the thermally induced magnetization fluctuations in a fine particle assembly should "smear" their anisotropic behavior. The smaller the particles, the greater the average deviation of the magnetization vectors with respect to the anisotropy and external magnetic fields.

In granular films and especially in granular multilayers, the interparticle distances are fairly small and comparable to the average particle size. Thus, the magnetic Co particles packed in the quasi-two dimensional arrays can be seen as strongly interacting ones. Dipole-dipole interactions lead to different internal fields at a single "probe" particle for the external magnetic field oriented in-plane or perpendicular to the film plane - a result of the shape anisotropy. Such a shape dependent anisotropy may be treated in a granular magnetic system within a mean-field approach [11]. The demagnetizing field may be expressed in terms of microstructure related parameters.

$$4\pi\tilde{M} = 4\pi<M> + \Delta N_p\left(\frac{<M^2>}{<M>} - <M>\right), \qquad (4)$$

where the first term is the average demagnetizing field of a particle assembly confined in the thin film geometry. The second term, having properties of uniaxial anisotropy field, originates from intrinsic shape anisotropy of a single particle described by the difference between its principal demagnetizing factors ΔN_p which is related to its aspect ratio. For a spherical particle $\Delta N_p = 0$ and for an infinitesimally thin disk-like particle $\Delta N_p = 4\pi$. $<M> = pM$, where p is the volumetric filling factor of Co particles.

If particles are small enough, a "static" FMR response characteristic of heterogeneous magnetic films with stable particles is strongly disturbed by thermally activated magnetization fluctuations. According to the theory of FMR in superparamagnetic particles [13], thermofluctuation effects lead to a reduction in the anisotropy (demagnetizing) field.

$$4\pi\tilde{M}(\xi) = 4\pi\tilde{M}\frac{1-\frac{3L(\xi)}{\xi}}{L(\xi)} = 4\pi\tilde{M}\frac{L_2(\xi)}{L(\xi)}, \qquad (5)$$

where $L(\xi)$ is the Langevin function with $\xi = m\omega/\gamma k_B T$ as a parameter which is proportional to the magnetic moment m of a single particle. It characterizes the influence of thermal fluctuations on the magnetic behavior of fine magnetic particles. k_B is the Boltzmann constant and T is the temperature.

It is fairly difficult to describe the joint effects of a particulate microstructure and thermally activated magnetization fluctuations on the FMR-line positions and FMR-line shape since the number of various parameters have to be known. These are the particle size, and its distribution, the particle shape, the filling factor, particle orientations and their distributions as well as the magnetocrystalline anisotropy. In principle, however, it is possible to achieve a reasonable description of the experimental FMR spectra in the framework of a modified Netzelman's model [15] for a system of interacting fine magnetic particles with superparamagnetic behavior. Dipolar interactions are described in the mean-field approach by Eq. (4) while the effect of thermal fluctuations is expressed by a term in Eq. (5) containing the Langevin function [13]. On the basis of our static magnetization data microstructure of the Co/Ag multilayers with $d_{Co} = 0.2$ nm may be characterized as arrays of the flat Co particles 1.6 nm in dismeter D, the average particle separation $b = 5$ nm ($p = 0.1$) and the thickness $t = 0.8$ nm and $\xi = 0.4$.

Accordingly, for a Co/Ag multilayers with $d_{Co} = 0.4$ nm, $\xi = 5$, $D = 4$ nm, $b = 9$ nm ($p = 0.2$) and $t = 1.4$ nm. Additionally, we assume that the Co particles are semicoherently oriented with the [111] (or [0001]) axis perpendicular to the film plane. Appropriate calculations, according to the Netzelmann's approach [14] with thermal fluctuations of the magnetization vectors taken into account give reasonable description of the FMR spectra: their line-positions and their lineshape [15]. This involves an additional contribution of the magnetocrystalline anisotropy of about 1×10^6 erg/cm^3 with the easy axis perpendicular to the film plane. The magnetocrystalline anisotropy of such a magnitude is in agreement with the value of 0.98 MJ/m^3 reported by Kingetsu [7] who attributed the smallness of this value to the crystallographic structure of Co with a random fcc/hcp stacking.

Having, in general, fairly well established the relationship between microstructural peculiarities of the granular Co/Ag multilayers and the ferromagnetic resonance, let us trace the effect of annealing on the FMR characteristics. Annealing of granular Co/Ag films or Co/Ag multilayers has been found to improve their GMR characteristics. It leads to (i) the growth of the already existing Co particles [1] or (ii) the changes in the microstructure of the Co layers from a continuous to a more discontinuous [3] and (iii) the transformation from fcc-like to the more hcp-like stacking either via post-annealing [2] or deposition at elevated temperatures [4].

Here we would like to explain the effect of annealing on the FMR spectra of the granular Co/Ag multilayers taking into account the specific changes both in the microstructure and in the crystallographic structure of Co. Fig. 5 shows the FMR spectra taken at the perpendicular configuration for the 100{0.3 nm Co/2.0 nm Ag} and the 67{0.6 nm Co/2.0 nm Ag} samples. The spectra were taken at 9.4 GHz at room temperature for the as-received and annealed at 400 °C for 15 min. For both as-received samples the FMR spectra are slightly asymmetric with a ratio of the amplitudes of the lobes above and below the base line different from 1. Upon annealing the shape of the spectra changes drastically. The lineshape becomes strongly asymmetric and the linewidth increases from about 1 kOe to about 2 kOe. The changes are more pronounced for the 67{0.6 nm Co/2.0 nm Ag}. To interpret these features one should recall that both the linewidth and lineshape of the FMR spectra of single domain particles are mostly related to the inhomogeneous broadening [16] due to a distribution of the easy axes and a magnitude of local anisotropy fields. Thus, the almost twofold increase in the linewidth can be partially explained by a substantial increase in the anisotropy. The appearance of the strong asymmetry in the lineshape can be attributed to a misalignment of the easy axes of Co particles. Apart from the changes in lineshape, a substantial lineshift upon annealing is observed. For the 100{0.3 nm Co/2.0 nm Ag} the FMR spectrum shifts upwards of about 1.5 kG and for the 67{0.6 nm Co/2.0 nm Ag} there is a downward shift in the line position of about 1.3 kG. To display the influence of annealing on FMR, we have chosen the spectra taken at the perpendicular to the plane configuration since the position of the FMR line in this configuration (see Eq. (3)) is directly related to the changes in the effective magnetization $\delta(H_r^{\perp}) = \delta(4\pi M_{eff}) = 4\pi M_{eff}^{as-dep.} - 4\pi M_{eff}^{anneal.}$.

Fig. 6 shows the changes in the effective magnetization $\delta(4\pi M_{eff})$ caused by annealing of Co/Ag multilayers versus d_{Co}. The most characteristic feature is a nonmonotonic behavior of $\delta(4\pi M_{eff})$ upon annealing depending on the nominal Co thickness d_{Co}. For low $d_{Co} < 0.4$ nm $\delta(4\pi M_{eff})$ is positive, then croses zero and eventually saturates below -1 kG for $d_{Co} > 0.6$ nm.

Any transition from the fcc to hcp stacking (with the c axis perpendicular to the film plane) is expected to lead to a decrease of $4\pi M_{eff}$ compared to the (111) fcc structure

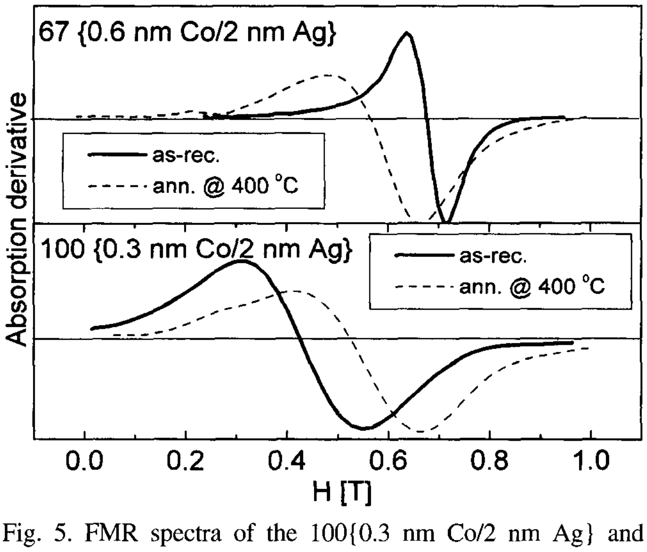

Fig. 5. FMR spectra of the 100{0.3 nm Co/2 nm Ag} and 67{0.6 nm Co/2 nm Ag} multilayers before and after annealing at 400 °C. The spectra were taken at the perpendicular to the film plane configuration.

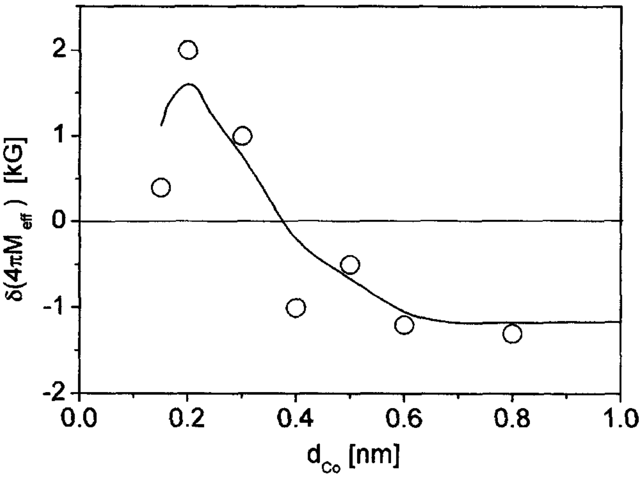

Fig. 6. Change in the effective magnetization due to annealing at 400 °C as a function of the nominal thickness d_{Co}. Solid line is the guide to the eyes only.

because of a higher value of K_U in the hcp structure. On the other hand according to Eq. (4), the changes in the microstructure can lead either to increase or decrease in demagnetizing field $4\pi\tilde{M}$ depending on the specific changes in the particle sizes or their shape. Let us consider the changes in $4\pi M_{eff}$ due to (i) an increase in $\delta(4\pi\tilde{M})$ which results from the growth of Co particles and (ii) a change in the uniaxial magnetocrystalline anisotropy $\delta(H_U)$ upon the transformation from the (111) fcc to (0001) hcp stacking.

$$\delta(4\pi M_{eff}) = \delta(4\pi\tilde{M}) + \delta(H_U) \qquad (6)$$

where any variation in the fourth-order anisotropy is neglected.

Taking into account the influence of thermally activated magnetization fluctuations [13] $\delta(4\pi\tilde{M})$ may be expressed as.

$$\delta(4\pi\tilde{M}) = \frac{\partial\left(4\pi\tilde{M}_\infty\frac{L_2(\xi)}{L(\xi)}\right)}{\partial\xi}\delta\xi, \qquad (7)$$

where $4\pi\tilde{M}_\infty$ is the demagnetizing field of an infinite, flat Co cluster and $\delta\xi$ is the increase in ξ parameter due to the growth of co particles.

As it was discussed above, in our Co/Ag granular multilayers annealing is expected to cause a similar structural transition as in Co/Mn system [9] but, again, the influence of the thermal agitation will smooth the increase in the uniaxial anisotropy especially for very fine Co particles. Hence, the change in the uniaxial magnetocrystalline anisotropy $\delta(H_U)$ may be roughly expressed as.

$$\delta(H_U) = \Delta H_U^\infty\frac{L_2\xi}{L(\xi)}, \qquad (8)$$

where ΔH_U^∞ is the change in uniaxial magnetocrystalline anisotropy field of an infinite Co cluster. Assuming $4\pi\tilde{M}_\infty$=17 kG for a continuous Co film and $\Delta H_U^\infty = -2$ kOe (a value comparable to the magnetocrystalline anisotropy field of -3.5 kOe evaluated for relatively thick Co layers in Co/Mn structures [9]), we calculated $\delta(4\pi M_{eff})$ as a function of ξ. The results of calculations are shown in Fig. 7. For the calculations we assumed, somehow arbitrary, a constant increase of the parameter $\delta\xi = 1$. This is an apparent oversimplification, but nevertheless, it reflects the general trend of the changes in the microstructure upon annealing for fine particle system. For $d_{Co} < 0.4$ nm the changes $4\pi\tilde{M}$ should be more pronounced due to the growth in particle size through precipitation of Co atoms or very fine clusters dissolved in the Ag matrix. By tracing the changes of the FMR intensity, we have checked that Co ultrathin layers of about 0.1 nm in nominal thickness are actually dissolved in the Ag matrix. On layers resulting in "rounding" of the Co islands with no appreciable change in their size. Only the small changes in $4\pi\tilde{M}$ are expected in a thickness range of $d_{Co} > 0.5$ nm since the lateral sizes of Co islands are large enough not to influence the magnitude of $4\pi\tilde{M}$. Comparing the results of calculations presented in Fig. 7 (solid line) with the experimental data points (Fig. 6), one finds that the general trend in $\delta(4\pi M_{eff})$ versus d_{Co} can be qualitatively explained.

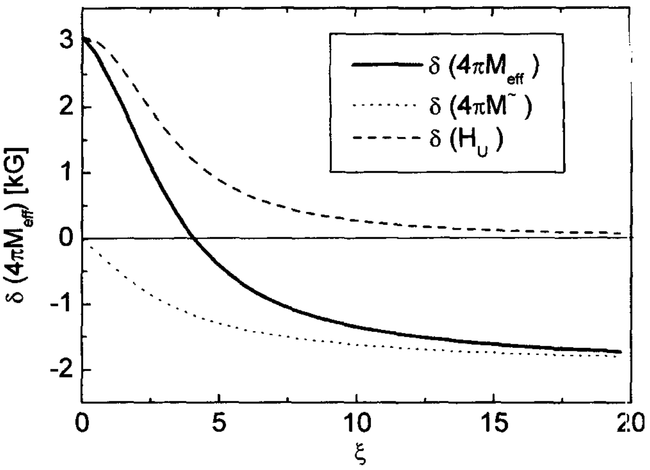

Fig. 7. Calculated (Eq. (2)) changes in the effective magnetization plotted as a function of the parameter ξ. Dotted and dashed lines represent the behavior of $\delta(4\pi\tilde{M})$ and $\delta(H_U)$, respectively.

4. Summary

We have investigated ferromagnetic resonance of Co/Ag multilayers with ultrathin Co layers. Due to negligible intersolubility with Ag, Co layers have an island-like microstructure and, for very low nominal thickness of Co ($d_{Co} < 0.4$ nm), they may be regarded as granular multilayers with flat, fine Co particles exhibiting superparamagnetic behavior. However, because the interparticle distances are fairly small, the dipole-dipole interactions are substantial-giving rise the non-zero effective magnetization $4\pi M_{eff}$ even for very small particles. The FMR spectra for such a system have been interpreted in the framework of a mean-field model of interacting anisotropic magnetic particles with thermally activated magnetization fluctuations. A stress has been put on the interpretation of the changes in the resonance spectra of the annealed samples. We have attributed the changes in the effective magnetization to Co-particles growth and to growth in the uniaxial anisotropy (perpendicular to the film plane) due to a structural transition from fcc to hcp atomic structure of the highly (111) textured Co particles.

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