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Magnetic properties of Fe and Ni nanoparticles formed in triethoxysilane films by ion irradiation or thermal processing

J.C. Pivin[1,a], E. Vincent[2], S. Esnouf[3], and M. Dubus[4]

[1] CSNSM-IN2P3, bâtiment 108, 91405 Orsay Campus, France
[2] SPEC-DRECAM, CEA Saclay, 91191 Gif-sur-Yvette, France
[3] LSI-DRECAM, CEA Saclay, 91191 Gif-sur-Yvette, France
[4] Centre de Recherche et de Restauration des Musées de France, 6 rue des Pyramides, 75041 Paris Cedex 01, France

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Abstract. Ion irradiation or heat treatments in vacuum of gel films prepared from mixtures of triethoxysilane with Fe and Ni nitrates permits to obtain a precipitation of metal particles in a glassy matrix, because these gels contain hydrido groups able to reduce Fe^{3+} and Ni^{2+} ions. The precipitation under irradiation is ascribed to the electronic excitations produced by the ions and the volume of metallic phase increases in proportion to the amount of energy transferred to electrons. The metal particles exhibit a narrower range of sizes than in films submitted to heat treatments in vacuum. Experiments of electron spin resonance indicate that the magnetic behavior of irradiated films is affected by a stress-induced anisotropy field. Films containing 3 to 7 at% Fe are in a superparamagnetic state in a given range of temperatures while the magnetic moments of nickel particles in films with similar metal contents exhibit a stronger correlation, due to a larger yield of precipitation and to the stress.

PACS. 61.82.-d Radiation effects on specific materials – 75.70.-i Magnetic properties of thin films, surfaces, and interfaces – 76.50.+g Ferromagnetic, antiferromagnetic, and ferrimagnetic resonances; spin-wave resonance – 75.50.Tt Fine-particle systems; nanocrystalline materials

1 Introduction

Sol-gel chemistry is a very convenient technique for producing nanomaterials with a wide range of magnetic and optical properties. The magnetic ordering in composite systems depends not only on the formed phases and particles volume fraction, but is also particularly sensitive to the size distribution and spatial dispersion of the particles. Thus the development of synthesis procedures permitting to control better these structural parameters is of major interest for applications. The nanostructure of composite ceramics obtained by heat treatments of gels is determined by the respective rates of hydrolysis and condensation of the gel precursor and of oxidation-reduction between components involved in the precipitation process. One of the authors demonstrated that ion irradiation is a more suitable means than thermal treatments for converting films of gels and inorganic polymers into ceramics with a low residual content of hydrogen, a high density and without cracks [1,2]. The gel derived from triethoxysilane ($SiH(OC_2H_5)_3$, hereafter labelled TH) constitutes an attractive matrix for metallic ions. Indeed the obtained gel, with the stoichiometry $SiO_{1.5}H_1$, is converted into silica containing silicon clusters by irradiation or annealing in vacuum [2,3]. Moreover, the hydrido group is able to reduce some metals at moderate temperatures in slightly reducing atmospheres (Ar:5%H_2) [4], while gels from tetraethoxysilane ($Si(OC_2H_5)_4$, labelled TEOS) containing same metals must be treated at high temperatures in pure H_2 [5,6]. Therefore, ion irradiation of gel films prepared from mixtures of TH with salts of magnetic metals may have an interesting issue. This paper reports a study of the structure and magnetic properties of TH films containing Fe or Ni and submitted to irradiation or heat treatments in vacuum. Its purpose is to show the interest of using the TH precursor for obtaining a metal precipitation and irradiation for optimizing the dispersion of the magnetic phase.

2 Experimental

Equal volumes of TH and ethanol were mixed and stirred during 1 h for permitting the hydrolysis of the ethoxide by the ambient moisture. Analysis of TH films by means of the nuclear reaction $^{12}C(d,p)^{13}C$ shows that the addition of water to the solution is not useful for hydrolyzing the Si-O-C_2H_5 bonds since the formed hydroxide contains less than 2 at.% C. The TEOS precursor was hydrolyzed with 3 moles of water per mole of TEOS, acidified with 10^{-2} moles of nitric acid, with stirring for 1 h before

[a] e-mail: pivin@csnsm.in2p3.fr

adding the metal salt. The nitrates $Fe(NO_3)_3{\cdot}9H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$ dissolved in ethanol were added to the gelling solutions, in molar ratios of 10% or 25% nitrate for 1 alkoxide. Films, with a thickness of the order of 500 nm, were deposited by spinning at a speed of 2000 rpm on silicon or silica substrates, depending on their subsequent use. Some of them were irradiated with incremented fluences of 3 MeV Au ions, in the range of 10^{13} to 10^{15}/cm^2, and others with 10^{16} He ions/cm^2 of energy 1.5 MeV, in order to determine if the precipitation is induced by electronic excitations or by atomic displacements. The nuclear stopping power of He ions is insignificant while that of Au ions is of 3.2 keV/nm and their electronic stopping powers are respectively of 0.3 and 3.0 keV/nm (adding the energies lost by the Au ions and the produced recoils). The density of deposited energy was constant throughout the thickness of the studied films and the ions were implanted in the substrate, at depths of 5 and 1 μm respectively for He and Au. It is worth to note that the evolution of H atoms and the crosslinking of bonds in a gel free of metal occurs at fluences of 10^{13} to 10^{14} Au/cm^2 or 10^{14} to 10^{15} He/cm^2 [2]. Other films were annealed for 1 h at temperatures, T, in the range of 873 to 1273 K in a vacuum of 10^{-6} torr. Multiple depositions with intermediate annealing at a same T were also performed for improving the statistics of experimental data and avoiding the flaking off of thick films.

The films composition after deposition and each type of treatment was characterized by means of Rutherford Backscattering Spectrometry (RBS), Nuclear Reactions Analysis of C and O atoms with deuterons (NRA) and Elastic Recoil Detection Analysis of H (ERDA). Their structure was studied by XRD at grazing incidence, using a Siemens diffractometer fitted with a Co anode. A few films were selected for TEM observations of their cross-sections, prepared by ion etching. Electron spin resonance (ESR), with a Bruker spectrometer operating at 9.8 GHz (X-band) and equipped with 100 kHz modulation, was used for studying the precipitation kinetics of the magnetic phases and the magnetization anisotropy of the films at room temperature (RT). In addition, measurements of the magnetization were performed as a function of the applied field, H, and temperature, T, with a SQUID magnetometer S600X from Cryogenic Ltd. Among the irradiated samples, only those having received the maximum Au fluence were studied by means of this technique. The procedure consisting in recording the variations of magnetization, M, under a constant field of low amplitude during heating, after zero field cooling (ZFC) or after cooling under the same field (FC), was used to investigate the interaction between magnetic domains [7]. Hysteresis loops $M(H)$ were also recorded at a few T.

3 Results

3.1 Characterization of the composition and structure

RBS analyses show that the depth distribution of M atoms (M = Fe or Ni) in as-deposited gels is homogeneous (whereas some other metallic salts tend to segregate at interfaces) and don't change after irradiation or annealing treatments. The atomic concentration ratio M/Si in pristine and treated films is the same as in the solution and the absolute concentration of M is of (3.0 ± 0.5) at.% or (7.5 ± 0.5) at.% after the release of H. The atomic concentration ratio O/Si in TH:M films is significantly larger than in films of pure TH (1.7 to 1.9 as against 1.5) because nitrate ions are introduced in the gel together with Fe or Ni. Nitrogen is removed after irradiation or annealing but not oxygen. The residual C content is of about 1 at.% whatever the treatment and the H content decreases down to 2 at.% after irradiation or annealing.

The broad features observed in the XRD diagrams of irradiated films seem to indicate that they are amorphous. These features are however centered at the same angles as the main diffraction peaks of the two metals in spectra of annealed samples. The lattice spacings of the crystalline Ni phase identified in TH:Ni films annealed in the range of T 873 to 1173 K are significantly different from those of the Ni_3Si silicide. But it is not possible to specify the composition of the bcc $Fe_{1-x}Si_x$ phase formed in TH:Fe films annealed in the same range of T, because the recorded peaks are broad and the lattice parameters of Fe and Fe_3Si are very close. Part of the particles are made of silicides Ni_2Si, Ni_3Si, FeSi and Fe_3Si in films annealed at 1273 K. No diffraction line of Ni or Fe oxides is detectable in spectra of TH:M samples. On the contrary, only NiO and α-Fe_2O_3 are identified in diffraction diagrams of TEOS samples annealed at 873 or 1273 K. Let us mention immediately that irradiated or annealed TEOS samples exhibit no magnetic response.

The precipitation of Fe, Ni particles is clearly evidenced by means of TEM in TH:M samples irradiated with He or Au ions (Fig. 1). Their size distribution is Gaussian, with a mean radius R_0 of 2.0 nm and a standard deviation σ of 0.4 to 0.6 nm in films containing 10% of Fe or Ni and irradiated with 10^{15} Au/cm^2. The particles number densities could not be estimated quantitatively because the thicknesses of the observed cross-sections were unknown, but this density appears to be significantly lower in TH:Fe films than in TH:Ni films for a same M content in solid solution in the gel and a same irradiation treatment. The size distribution in annealed samples is broader and better fitted with a log-normal function, centered at 3 nm and of width σR_0 equal to 4 nm for films annealed at 1273 K (Fig. 2). Porosities and regions of lower density are also observed in images of annealed films (light areas in Fig. 2) while irradiated films are generally more dense.

3.2 Magnetic properties

The results of magnetometry experiments at different temperatures are presented at first for defining the magnetic state of films, because ESR spectra were recorded only at RT. The variation of M with T under a low field of 50 Oe, displayed in Figure 3a for a TH:3%Fe film irradiated with Au ions is typical of a superparamagnetic system [7] or of a spin glass [8] (the behavior of a film

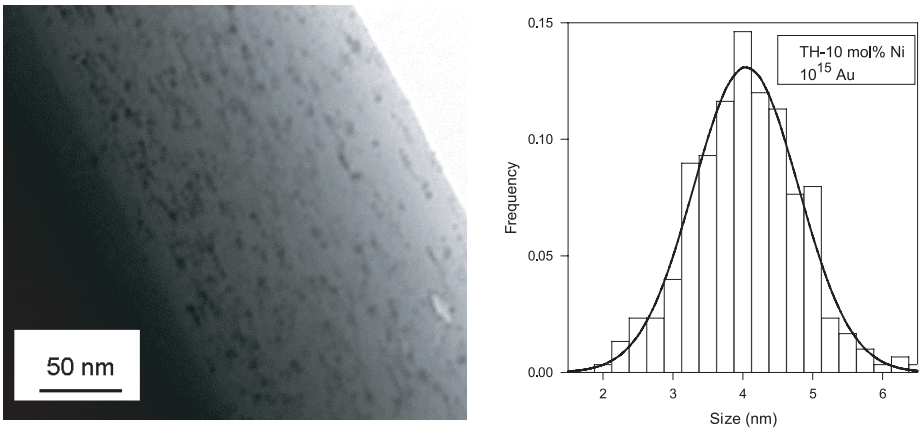

Fig. 1. Cross-section of a TH:Ni film irradiated with 10^{15} Au ions/cm^2, histogram of sizes and fit of this histogram with a Gaussian function of which parameters are given in the text.

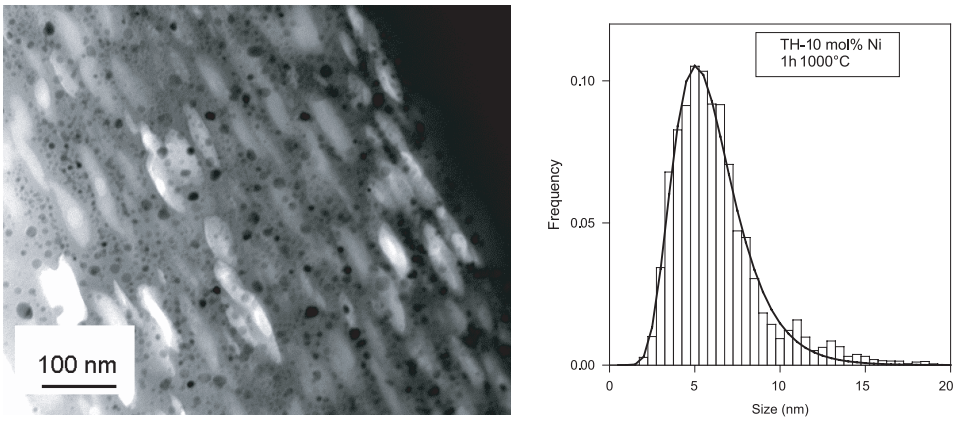

Fig. 2. Cross-section of a TH:Ni film annealed at 1000 °C, histogram of sizes and fit with a log-normal function. White areas are supposed to be porosities and light grey areas regions with a lower density. The metal particles are darker than the matrix and rounded.

containing 7 at.% Fe is similar). Finite remanence and coercivity are also observed in hysteresis loops M versus H below 45 K. It is well known that, when the mutual dipolar interaction between single-domain ferromagnetic particles is insignificant, the orientation of each "superspin" remains blocked after zero field cooling parallel to one of the easy magnetization axes of the particle, independently of the other particles. These superspins become able to flip between easy directions during the experiment above a "blocking temperature" T_b, which is related to their anisotropy energy barrier E_b. In the case of a collection of nanoparticles with a narrow range of sizes, a maximum is observed at the mean T_b value in the ZFC curve and the system appears to be in a paramagnetic state at higher T. A collective freezing, like in a spin glass below a "glass temperature" T_g (equivalent to the T_b of isolated particles), cannot be ruled out in the case of presently studied films without performing measurements of ac-susceptibility or experiments of memory imprinting at intermediate temperatures between T_g and 4 K [8]. But the volume fraction of particles would be of the order of 2.5 or 6.5% in these TH:Fe films (a little smaller than the atomic concentration), if all the metal atoms were precipitated, and in this case the inter-particle distance would be of the order of 5 times their size, taking into account the sizes measured in TEM. Moreover, values of saturation magnetization (see below) indicate that only 10% of the Fe atoms are in the precipitates formed in irradiated films. Established rules [9] and Monte Carlo simulations [10] predict a magnetic correlation between Fe or Ni particles when their volume fraction reaches 10−15%. The FC and ZFC magnetization curves of the TH:Fe irradiated films are approximately described by a Curie law (shown with a continuous line in Fig. 3) at T above T_b. The agreement with a Curie-Weiss law is not better. One can suppose that $M(T)$ curves recorded under fields lower than 50 Oe would follow better the Curie law (because $M(H)$ curves exhibit an inflexion point around 200 Oe), but the order of magnitude of the magnetization of TH:M films, with a volume of 10^{-5} cm^3, becomes too small for performing measurements with a good statistics.

The mean size of particles in superparamagnetic systems is commonly estimated from the T_b value, by using the Stoner-Wohlfarth model [7,11]. For non interacting

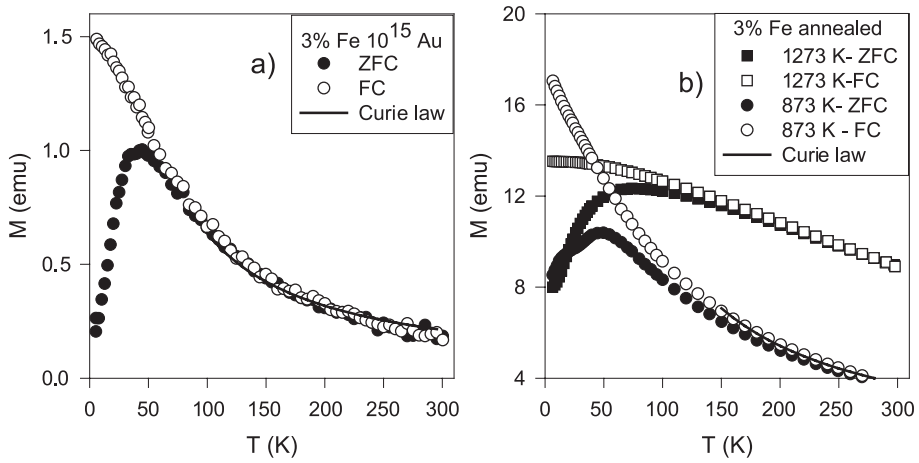

Fig. 3. ZFC and FC magnetization curves under an applied field of 50 Oe of a) a TH:Fe film containing 3 at.% Fe irradiated with 10^{15} Au ions/cm^2; b) TH:Fe films containing 3 at.% Fe annealed at 873 and 1273 K. The magnetization values are multiplied by 10 for the film annealed at 873 K.

particles with randomly distributed anisotropy axes, the approximate expression of the mean activation energy of spin rotation is:

$$E_b = KV(1 - HM_s/2K)^{1.5} \tag{1}$$

in which K is the anisotropy factor of the particles, V their volume and M_s the saturation magnetization of the magnetic phase. The relaxation time τ of the system is given by the Arrhenius law:

$$\tau = \tau_0 \exp(E_b/kT). \tag{1b}$$

The angular inverse attempt frequency τ_0 is typically of $10^{-8} - 10^{-10}$ s and τ becomes comparable to the measurement duration, of 10^2 s with a SQUID, at a temperature $T_b \sim KV/25k$. Assuming that (i) all the metal is precipitated in the film of Figure 3a, (ii) the particles are made of pure iron and (iii) their anisotropy is of crystalline nature, a mean radius of 4 nm is deduced from the T_b value. This size is twice as large as the mean radius measured in TEM and a smaller size, of 1.5 nm, is also found from the expression of the Curie constant. This discrepancy will be analyzed further on, taking into account other measurements on similar films.

Contrary to Fe particles, Ni particles in irradiated films don't exhibit a blocking of their spin after zero field cooling nor a variation of their magnetization as $1/T$. The FC magnetization of these films under fields of 50 or 100 Oe is larger by about 25% than their ZFC magnetization at low T and both decrease by a factor 2 between 5 K and 300 K. The shape of the curves, shown in Figure 4, seems to indicate that a little part of the system is in a paramagnetic state. This paramagnetic contribution is not that of defects in the matrix, because the magnetic response of a TH film containing no metal and submitted to the same irradiation is smaller and independent of T.

Figure 3b shows that the FC curve of a film containing 3 at.% Fe and annealed at 1273 K exhibits an inverse curvature with respect to the curve of a paramagnetic sample.

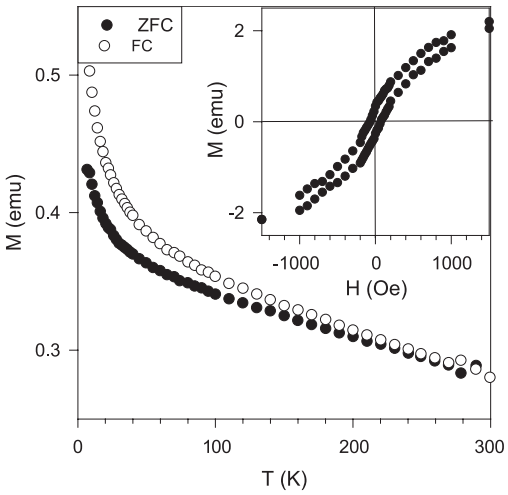

Fig. 4. ZFC and FC magnetization curves under an applied field of 50 Oe of a TH:Ni film containing 3 at.% Ni irradiated with 10^{15} Au ions/cm^2. The inset shows the hysteresis loop recorded at 50 K.

The variation law, as $M_0\,(1 - KT^{3/2})$, of the FC magnetization in this film and all the others containing Fe or Ni annealed at same T is of same type as that of the saturation magnetization of the bulk metals, with however larger values of K factor. This shape together with the small decrease of the FC magnetization between 5 and 300 K, indicate that these films are ferromagnetic. In addition, $M(H)$ curves exhibit an hysteresis up to 300 K and the saturation magnetization M_s decreases by only 30% with the increasing T. However, the ZFC magnetization of these films, under applied fields 10 times lower than their coercive field H_c, deviates from the FC value below 50 K (by about 50% at 5 K). Thus a little part of the particles system is superparamagnetic at high T. It is worth to note that the moments of the largest particles observed in TEM should be unblocked at 285 K if there was no magnetic coupling. The magnetic response of films annealed for 1 h at 873 K is superparamagnetic at high T

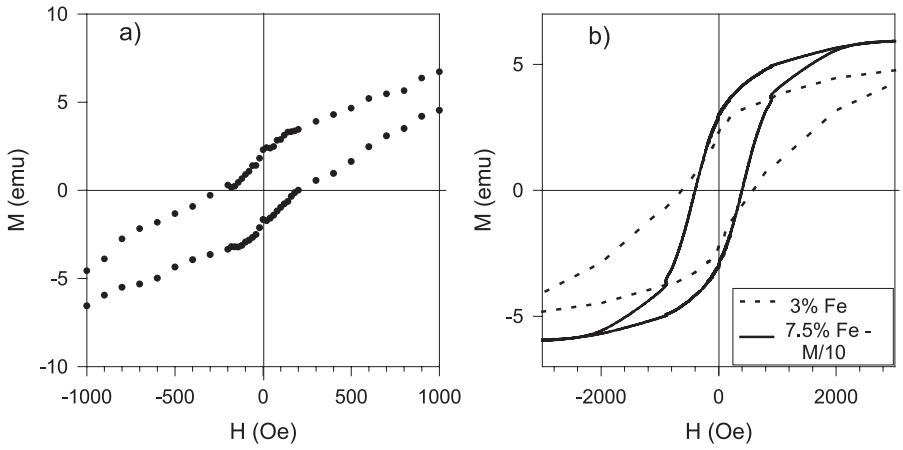

Fig. 5. Hystereses of magnetization at 5 K of a) a film containing 3 at.% Fe irradiated with 10^{15} Au ions; b) TH:Fe films with 2 Fe contents annealed at 873 K. The magnetization values are divided by 10 for the film containing 7.5 at.% Fe.

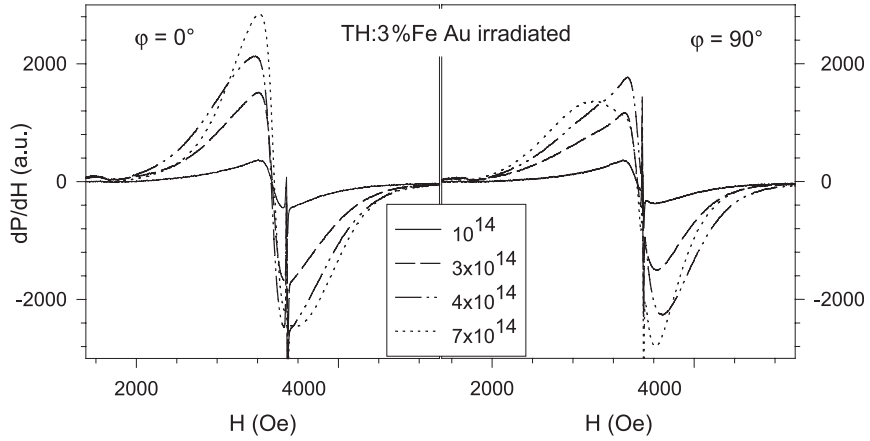

Fig. 6. ESR spectra of TH:Fe films containing 3 at.% Fe and irradiated with the indicated fluences of Au ions for 2 orientations φ of the film surface with respect to the applied field.

(Fig. 3b), but the ZFC magnetization of these films tends progressively towards the FC value above T_B. This behavior is typical of materials containing particles with a broad range of sizes and is in agreement with TEM observations of same films. The broadening of the size distribution in films annealed for a longer time at 873 K (case of multiple depositions with intermediate annealings) or for 1 h at T between 873 and 1273 K makes that some particles are progressively unblocked in the whole range of T of the measurements.

Values of the saturation magnetization measured at 5 K correspond to precipitated fractions of only 1/10 of the Fe atoms and 1/2 of the Ni atoms in films irradiated with 10^{15} Au ions (the maximum value of M_s being equal to that of the bulk metal multiplied by a volume fraction f of metal phase deduced from the atomic fraction measured in RBS). The difference of Fe and Ni precipitated fractions estimated from magnetization measurements corroborates the results of TEM observations. The precipitation yield of metal phase in annealed samples increases with the temperature and duration of treatments, as also with the metal concentration, on basis of the few data available. It is comparable to that in heavily irradiated samples after a treatment of 1 h at 873 K and a noticeable part of the Fe atoms are still in solution in the oxide after a treatment for 1 h at 1273 K.

The shape of the hysteresis loops indicates that the metal particles are not encapsulated in shells of antiferromagnetic oxide, containing the remaining part of the M atoms. Indeed, a shift of the loop center along the field axis would be observed if that was the case [12]. Examples presented in Figure 5 show that the absolute values of coercive field, H_c, and residual magnetization, M_r, which are measured under positive and negative fields are equal within 10%. Note also that the coercive fields are in the range of 200 to 600 Oe for all the studied films and H_c tends to decrease with the temperature and duration of annealing treatments, in correlation with the increasing size of particles [13,14].

ESR spectra of irradiated TH:M films on silica substrates exhibit a sharp peak at 3495 Oe (corresponding to a spectroscopic splitting factor g of 2.00), ascribed to the E' centers created in the glassy matrix and substrate. A ferromagnetic resonance becomes detectable for a fluence of 10^{14} Au ions/cm^2, as shown in Figure 6 for a film containing 3 at.% Fe. The peak to peak height of the derivative of absorbed power P with respect to the applied dc field H, dP/dH, increases with the ion fluence. The peaks

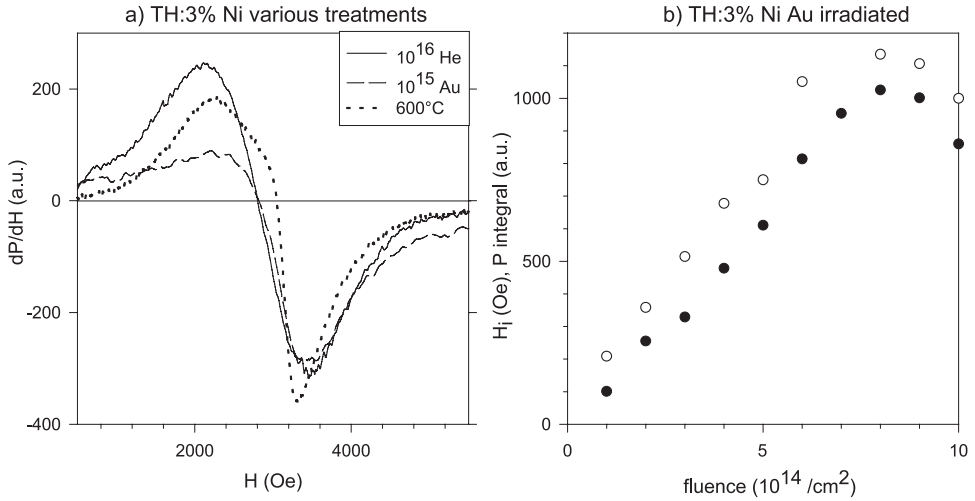

Fig. 7. a) ESR spectra of TH:Ni films containing 3 at.% Ni submitted to various treatments and (b) variations of the internal field and integral of absorbed power with the fluence of Au irradiation.

being often asymmetrical, the usual procedure consisting to multiply the peak height by the square of its width for evaluating the total absorbed power P was not used. The integral of $P(H)$ was calculated by double numerical integration and normalized by the sample area. This integral increases more or less linearly with the fluence of Au ions up to 8×10^{14} (Fig. 7). Very comparable values of P integral are measured for a same metal content in TH:Fe films irradiated with 8×10^{14} Au or 10^{16} He ions and a five times larger value is measured in the case of the He irradiation for TH:Ni films submitted to same treatments. One can conclude from this result that electronic excitations are responsible for the reduction of Fe^{3+} and Ni^{2+} ions by Si atoms with dangling bonds, following the breaking of the hydrido group, and that the segregation of neutralized atoms requires little activation. Indeed, atomic displacements produced by heavy ions contribute mainly to precipitation processes in other systems by enhancing the amount of defects liable to migrate.

Another quantity which is proportional to the volume fraction of metal is the demagnetizing field H_d. Its value is related to those of resonance field, H_r, (intersect of the derivative curve with the base line) and of effective precession field, H_0, by well known formula when the magnetic moments are homogeneously distributed in a thin film and the magnetic energy is the sum of only the Zeeman and magnetostatic energies. For a given angle φ of the applied d.c. field H with respect to the surface, the relationship is:

$$H_0^2 = \left(\frac{2\pi\nu_0}{\gamma}\right)^2 = (H_r + H_d \cos 2\varphi)(H_r - H_d \sin^2 \varphi) \quad (2)$$

where ν_0 is the resonance frequency of the cavity, γ the gyromagnetic ratio of the ferromagnetic electrons ($\gamma = g\beta/\hbar$, β being the Bohr magneton) and H_0 the effective precession field. This law describes very well the anisotropy of annealed films and of TH:Ni irradiated films (Fig. 8), with g factors of (2.07 ± 0.01) and (2.35 ± 0.05) for TH:Fe and TH:Ni samples respectively, as against 2.10 and 2.21 for bulk metals. The agreement is less satisfactory for TH:Fe irradiated samples (Fig. 8). In other respects, values of the magnetization, $M = H_d/4\pi$, deduced from same fits, are noticeably smaller than the product of the saturation magnetization of the bulk metal M_s^b by the maximum

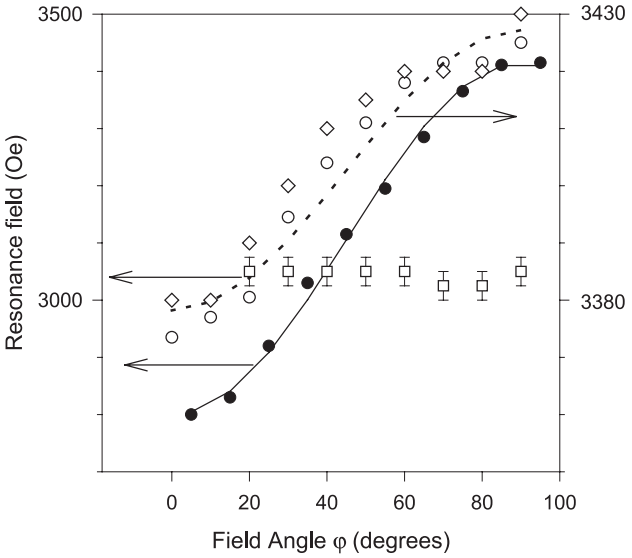

Fig. 8. Resonance anisotropy of films irradiated with 10^{15} Au ions/cm^2: (full circles) TH:3%Ni, (open symbols) TH:3%Fe. The continuous line shows a fit of the Ni resonance by using formula (2) with $g = 2.29$ and an apparent magnetization $M\,(H_i/4\pi)$ of 70 emu and the dotted line shows a fit of the mean resonance field of Fe particles with $g = 2.06$ and $M = 3$ emu. The mean resonance field of Fe particles is plotted with open circles and the position of peak (I) with open rhombs, that of peak (II) with open squares and the error bars indicate the uncertainty on Lorentzian fits. The field scale for the Ni resonance and the resonance peak (II) of Fe is on the left and that for the mean resonance and peak (I) of Fe on the right.

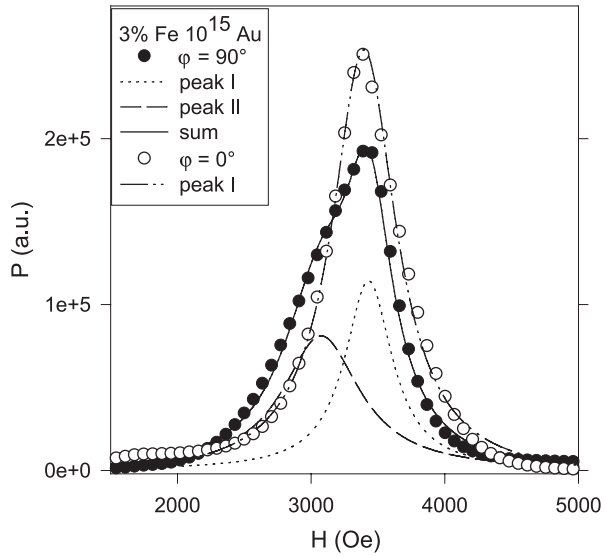

Fig. 9. Integrated resonance peaks $P(H)$ from a TH:3% Fe film irradiated with 10^{15} Au ions/cm^2 for 2 orientations of the surface φ (symbols) and fits (lines) by either a sum of 2 Lorentzian functions, labelled peak I and II, or a single function for $\varphi = 0$.

volume fraction of metal f for all TH:Fe films (10 times for samples irradiated with Au ions), but they reach the maximum value $f \times M_s^b$ for TH:Ni films annealed at 873 K and exceed this value by a factor of 2 to 4 for irradiated TH:Ni films. The result concerning films with Fe seems reasonable since magnetometry experiments also show that only a part of the Fe atoms is precipitated and these films are superparamagnetic at RT. However, a more detailed analysis of the peak shape indicates that equation (2) does not apply to most of the TH:Fe films because their magnetization is not homogeneous. Indeed, $P(H)$ curves in TH:Ni samples can be generally fitted by a single Gaussian function or, in the case of some annealed samples, by a sum of 2 Gaussian functions of which centers exhibit the same dependence on angle φ. On the contrary, two defined peaks are often observed in the raw spectra, dP/dH, of TH:Fe films (for fluences higher than 3×10^{14} in Fig. 6) and $P(H)$ peaks can be fitted only by a sum of two Lorentzian functions (Fig. 9). In addition, only the resonance field of the peak with an "effective g factor" ($h\nu_0/\beta H_r$) close to 2.0, labelled (I), obeys approximately equation (2) as shown in Figure 8. The second peak, labelled (II), is centered at a field value independent of φ and corresponding to a larger g factor (2.2 to 2.4). Only the peak (I) is observed in spectra of samples irradiated with a low ion fluences whatever the angle φ and in spectra recorded with $\varphi = 0°$ for large fluences (Fig. 9). The magnitude of peak (II) increases with the angle φ and with the fluence, but it still contributes for less than 35% to the total area of the resonance for $\varphi = 90°$ after irradiation with high fluences or heat treatments, with the result that the resonance field estimated from the derivative of the sum obeys approximately equation (2).

4 Discussion

The splitting of Fe resonance peaks and the high internal fields of TH:Ni films are ascribed to the contribution of an anisotropy term to the magnetic energy. In the case where crystallites in a planar film exhibit a significant exchange or magnetostatic coupling and the anisotropy axis is the normal to the surface, the anisotropy field H_a can simply be added to H_d in equation (2) [15,16]. This seems to be the case for TH:Ni films, probably because the magnetostatic coupling between Ni nanoparticles is strong enough, due to a larger precipitation yield than in TH:Fe films. When the crystallites in a superparamagnetic film (without coupling) are spherical and undergo a same anisotropy field H_a, its effect on the resonance of the ensemble is the same as that of a preferential orientation of the crystallites: a shift by $\pm H_a$ with respect to H_0. The anisotropy is not of crystalline origin in present case, because TEM observations with high resolution show that the lattice orientation of the nanoparticles is isotropic. It is not either related to a change of coordinence at the surface, since the particles are embedded in films with a thickness of a few hundreds nanometers. Therefore, it is supposed to be induced by the stress resulting from the athermal processes of compaction and precipitation. A change of anisotropy induced by magnetostriction has been observed in single-phased magnetic films after heavy ion irradiation [17]. Taking that the internal field, $H_i = H_d + H_a$, obeys equation (2) and is larger than $4\pi \times f \times M_s^b$ in TH:Ni films, the stress is probably isotropic in the film plane and the product $\lambda\sigma$ of the magnetostriction factor by the stress is positive [16]. It is worth to note that, in the TH:Ni irradiated films, H_i increases in proportion to the ion fluence as the absorbed power (Fig. 7b) but it cannot be used for assessing the precipitation kinetics because there is no reason to suppose that the term H_a is proportional to the precipitated fraction of metal.

The heterogeneous broadening (Gaussian shape) of Ni resonance peaks, which is typical of disorder, seems to indicate that either the stress or the magnetization exhibits strong fluctuations [15]. The observed widening of the Ni resonance peaks with the increasing fluence in Au irradiated films is ascribed to the increase of atomic damaging. The decrease of both the internal field and the P integral for Au fluences above 8×10^{14} is also most probably due to a redissolution of the particles under the effect of collision cascades. In the case of TH:Fe films, a noticeable part of the particles appears to be unaffected by the stress (peak (I)) and, according to our hypothesis, peak (II) corresponds to the particles experiencing stress. Angular scans indicate that the anisotropy field of the latters is perpendicular to the surface. This difference with respect to Ni particles can be explained by the opposite signs of λ for the 2 metals [18]. In addition, the intensity ratio of peaks (I) and (II) indicates that the proportion of stressed particles increases with the ion fluence, but particles of type (II) remain in minority at high fluence and the mean resonance field still follows approximately equation (2). The lower mean stress than in TH:Ni films and the almost constant stress experienced by part of the Fe

particles (according to their constant resonance field) are most probably due to the smaller precipitation yield of Fe (attested by the superparamagnetism of TH:Fe films). It seems that damaging has not either the same effect in TH:Fe and TH:Ni films since the width of Fe resonances varies less with the ion fluence and their shape is nearly Lorentzian (homogeneous widening).

In addition to the shape and position of resonances, the predominance of the stress-induced anisotropy over the crystalline anisotropy in irradiated films explains the larger sizes of particles deduced from blocking temperatures than from Curie constants or than those observed in TEM images. Formula (1) should be used instead for estimating the anisotropy factor $K \sim 3\lambda\sigma/M$ for particles with a mean radius of 1.5 to 2.0 nm in the case of the irradiated film of Figure 3a.

Other authors performed magnetization measurements only on monoliths and powders prepared by the sol-gel route, while the properties of films are more interesting for applications in computer technology. Amorphous oxyhydroxides or nanocrystals of fayalite and magnetite are generally formed when treating TEOS:Fe gels in hydrogen atmosphere at T in the range of 800 to 1000 K [5,6,19] (a reduction of iron is however feasible by using ligands). Similarly, treatments of TEOS:Ni gels in hydrogen give mixtures of NiO and Ni particles with oxide shells [20], exhibiting intricate magnetization hystereses. Precipitations of 3d magnetic metals in thin dielectric films are more easily obtained by vapor, sputtering or cluster beam deposition [21–25] or by combining ion implantation with heat treatments in hydrogen [26–28]. However, in vapor-deposited and sputtered films the particles tend to be located preferentially at the boundaries of matrix columns, which are typical of such films, and to coalesce for lower M contents than in films with a random distribution of particles. The spatial and size distributions are more homogeneous in cluster beam deposited films. It may be worth to note that a transition from a superparamagnetic to a ferromagnetic state was observed in this type of films for volume fractions of metals of the order of 20% and correlated to the percolation of particles with a controlled size of 3−5 nm [21] (whereas they tend to grow in annealed TH:M films). The transition occurs for similar concentrations of metal in implantation films but the main characteristics of this type of films are the heterogeneity of magnetization induced by the Gaussian distribution of implanted atoms. That's why ion irradiation of unstable systems is an interesting alternative for synthesizing colloid films with a defined size, an homogeneous spatial distribution of the particles, as also at a lower cost because 100−1000 times smaller ion fluences are used for obtaining similar volume fractions of metal. This goal was attained by combining the reduction ability of hydrido groups in the TH gel with the radiolysis of these groups by electronic excitation. We must admit that the magnetic properties of the irradiated films are complicated by their anisotropy, which depends on the density of particles and on the irradiation conditions. The exact nature of this anisotropy needs to be confirmed, for instance by performing experiments of irradiation followed by annealing treatments at low T or the reverse. The magnitude and sign of the stress are also unknown. The particles in TH:M films are supposed to undergo a planar compression for the following reasons. Nanoparticles embedded in a matrix are generally submitted to a compression (isotropic and increasing in inverse proportion to their size) under the effect of the interfacial stress [29,30] and the magnetization anisotropy of particles in some sputtered films has been ascribed to this stress [25]. An additional compression arises from the compaction and precipitation processes in gel films. On the other hand, heat treatments of pristine TH:M films in vacuum are also suitable for obtaining superparamagnetic systems. The temperature of the treatment must be limited to 800−1000 K for avoiding the broadening of the particles size distribution and the formation of silicides. The magnetization per Fe or Co atoms in silicides is known to decrease with the Si concentration (they become non-magnetic for a concentration of about 50 at.%), because of the weakening of the exchange coupling [31], and this is also probably true for Ni silicides.

5 Conclusions

Ion irradiation of TH gels containing Fe or Ni ions leads to the formation of metal particles, essentially under the effect of electronic excitations. These excitations provide the activation energy of the reduction of M ions by Si atoms with dangling bonds, following the radiolysis of hydrido groups (occuring at lower fluences [2]). This athermal process offers the advantage of obtaining particles with a narrower range of sizes than heat treatments. In addition, they are free of oxide shell, despite the detrimental effect of ballistic mixing, by the shape of magnetization loops. The progressive increase of the magnetization evidenced by ESR experiments seems also to indicate that the particle size and number density can be tailored through the ion fluence.

The preliminary investigation of ferromagnetic resonances in these films shows that the technique is a relevant means to investigate the precipitation kinetics of magnetic phases, especially when the particle sizes are at the limit of the resolution of TEM. One must however take into account carefully local variations of magnetization correlated to stress or other interfacial effects and the resolution of equations relating the resonance field to the internal field becomes complicated.

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