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Magnetic behavior of Fe:Al₂O₃ nanocomposite films produced by pulsed laser deposition

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Structured nanocomposite films consisting of five Fe layers embedded in an amorphous Al₂O₃ matrix (Fe:Al₂O₃) have been grown by sequential pulsed laser deposition. The formation of well isolated quasispherical nanocrystals is observed for samples with Fe content per layer close to 6.5×10^{15} atoms/cm². Increasing the Fe content leads first to the formation of elongated nanocrystals and then to quasicontinuous layers. The evolution in the shape and size of the nanocrystals is reflected in the magnetic behavior of these systems. A crossover from a low temperature ferromagnetic regime to a high temperature superparamagnetic regime is observed at a temperature of 23 K in the samples containing isolated quasi-spherical nanocrystals. In this case, a reduced moment per Fe atom ($1.4 \mu_B$ /atom) with respect to the value for α -Fe ($2.2 \mu_B$ /atom) is estimated. This behavior is attributed to the presence of a Fe-oxide surface shell on the nanocrystals. The large values of the estimated effective magnetic anisotropy (1.4×10^6 J/m³) and the low temperature coercivity in these samples are attributed to a strong surface contribution to anisotropy, whereas the temperature dependence of coercivity is attributed to thermal activation. © 2001 American Institute of Physics. [DOI: 10.1063/1.1415054]

I. INTRODUCTION

The physical properties of nanocomposite materials consisting of metallic nanocrystals (NCs) embedded in a dielectric matrix greatly differ from their respective bulk materials. They depend not only on the choice of NC and matrix materials but also on the size, shape, and surface effects related to the small nanocrystal size.^{1–5} These materials present very interesting electrical, optical, or magnetic properties that are of potential interest in different applications. Noble metal (Au, Ag, and Cu) NCs embedded in matrices such as SiO₂ or Al₂O₃ present selective absorption related to the appearance of surface plasmon resonances^{4,6,7} and enhanced values of the third order nonlinear optical susceptibility,^{4,6,8} that make them candidates for the development of both passive and active optical devices such as integrated polarizers^{4,9} or all-optical switches.^{6,10} Nanocomposites containing magnetic metal (Fe, Co, and Ni) NCs are characterized by interesting magnetic effects such as possible quantum tunneling of magnetization¹¹ or giant magnetoresistance.¹² They are potential candidates for ultrahigh density magnetic recording media,^{13,14} though superparamagnetism places a lower limit on the size of useable NCs.¹⁵ The development of synthesis

methods allowing a good control of the nanocrystal size, shape, and distribution is thus of great technological interest.

Several deposition methods have been used to produce nanocomposite materials containing magnetic NCs such as sol-gel,^{16,17} sputtering,^{18–21} ion implantation,^{22,23} or pulsed laser deposition (PLD).^{24–26} Among them, PLD is one of the most promising methods since it is a single step process that allows the sequential and independent deposition of the metallic NCs and the matrix, and therefore, should allow the nano-engineering of optimized structures. In the present work, Fe:Al₂O₃ nanocomposite films were produced by PLD. The evolution of the morphology of the deposited Fe from small isolated NCs to quasi-continuous layers is studied. The combined use of structural [high-resolution transmission electron microscopy (HRTEM) and Rutherford backscattering spectrometry (RBS)] and magnetic characterization techniques allows us to elucidate the structure of the Fe NCs and the surface state of the NCs. The magnetic response of the nanocomposite films is discussed in terms of effective anisotropy for the samples containing isolated quasi-spherical NCs in which a superparamagnetic regime is observed at high temperatures.

II. EXPERIMENT

Nanocomposite films consisting of Fe layers dispersed in an amorphous Al₂O₃ matrix (Fe:Al₂O₃) have been prepared

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TABLE I. Sample name, experimental synthesis conditions, Fe areal density per layer ($[\text{Fe}]$), and total thickness of the $\text{Fe}:\text{Al}_2\text{O}_3$ nanocomposite films as determined from compositional analysis (RBS).

Sample	No. of pulses on Fe per layer	$[\text{Fe}]$ ($\times 10^{15}$ atoms/ cm^2)	Thickness (nm)
FE065	100	6.5	135
FE095	150	9.5	135
FE130	200	13.0	145
FE145	250	14.5	140
FE195	300	19.5	140
FE245	400	24.5	140

by sequential PLD in a vacuum (1×10^{-6} mbar). A pulsed ArF excimer laser [$\lambda = 193$ nm, $\tau = 20$ ns full width at half maximum, and 5 Hz repetition rate] was alternatively focused at an angle of 45° on the surface of high purity Fe and alumina targets to lead to an energy density of $1.5 \text{ J}/\text{cm}^2$, which is above the ablation threshold of both targets. The synthesis process consisted of the sequential deposition of an Al_2O_3 layer followed by the deposition of a layer of Fe. The effective thickness of the Al_2O_3 layers and the Fe content in the samples were controlled by varying the number of laser pulses on each target. In the present work, an approximate effective thickness of 20 nm was chosen for the Al_2O_3 layers, whereas the number of pulses on the Fe target was varied in the range 100–400 in order to study the evolution of the morphology of the deposited Fe layers from well isolated NCs to quasi-continuous layers.

The nanocomposite films were grown either on Si or carbon-coated mica (c-mica) substrates for magnetic and structural analysis, respectively. The substrates were positioned 32 mm from the target along the direction perpendicular to the target and maintained at room temperature during deposition. In the case of the films grown on Si, the growth sequence was repeated five times and was followed by the deposition of an Al_2O_3 capping layer to protect the Fe NCs. Films grown on c-mica had a simple sandwich structure $\text{Al}_2\text{O}_3/\text{Fe NCs}/\text{Al}_2\text{O}_3$ to facilitate the structural analysis.

The areal density per layer of Fe ($[\text{Fe}]$) in the samples was determined by RBS using a 2.0 MeV $^4\text{He}^+$ beam and the experimental spectra were simulated by means of the RUMP program.²⁷ The number of pulses used to grow the Fe layers, $[\text{Fe}]$ and the total thickness of the $\text{Fe}:\text{Al}_2\text{O}_3$ films as determined from the compositional analysis are shown in Table I. Note that the samples are named according to their Fe areal density. The morphology and structure of the films have been investigated with in-plane view by HRTEM using a JEOL 4000EX transmission electron microscope operated at 400 kV (point to point resolution ≈ 0.16 nm). Magnetic properties of the deposited samples were measured in the plane of the sample in the temperature range 2–300 K using a high sensitivity (10^{-6} emu) vibrating sample magnetometer with a maximum applied magnetic field of 2 T. The temperature dependence of the magnetization after field cooling (FC) and zero-field cooling (ZFC) was measured to determine the blocking temperature (T_B), while hysteresis loops, $M(H)$, were measured at different temperatures to determine the

FIG. 1. HRTEM images of nanocomposite samples grown with increasing $[\text{Fe}]$: (a) 6.5×10^{15} atoms/ cm^2 (FE065), (b) 9.5×10^{15} atoms/ cm^2 (FE095), and (c) 13.0×10^{15} atoms/ cm^2 (FE130).

temperature dependence of the saturation magnetization and coercivity in the various samples.

III. RESULTS

Figure 1 shows HRTEM images of samples grown with increasing $[\text{Fe}]$: (a) 6.5 (FE065), (b) 9.5 (FE095), and (c) 13.0×10^{15} atoms/ cm^2 (FE130). The dark areas in the images of Fig. 1 correspond to the Fe NCs, whereas the background corresponds to the amorphous Al_2O_3 matrix. The nanocomposite sample with the lowest $[\text{Fe}]$, FE065, consists of a homogeneous distribution of NCs of quasi-circular cross section with an internanocrystal spacing close to the in-plane diameter of the NCs [Fig. 1(a)]. As $[\text{Fe}]$ increases, the NC morphology is significantly altered. For an intermediate $[\text{Fe}]$, FE095, a mixture of NCs of circular and elongated cross section co-exist [Fig. 1(b)], while for higher $[\text{Fe}]$, FE130,

FIG. 2. In-plane average NC dimensions as a function of $[\text{Fe}]$ in the nano-composite films. Results are included both for the NC length ($\circ$) and breadth ($\bullet$). The bars correspond to the standard deviation, whereas the vertical dashed line qualitatively indicates the critical $[\text{Fe}]$ at which the NCs form a quasicontinuous layer.

quasicontinuous networks of long Fe chains [Fig. 1(c)] are observed. For even higher $[\text{Fe}]$, coalescence leads to the formation of quasi-continuous Fe layers.

The average dimensions of the NCs, length, L and breadth, B , estimated from analysis of the images of the films shown in Fig. 1 are given in Fig. 2 as a function of $[\text{Fe}]$. The bars included in Fig. 2 correspond to the standard deviation of the average NC length and breadth. It is seen that $L \approx B$ for the NCs observed in FE065 and, thus, we can consider that the Fe NCs have quasi-circular cross sections with an average diameter $d_{\text{av}} \approx 2.2$ nm. In addition, this sample shows a narrow distribution in particle diameter. As $[\text{Fe}]$ increases, the NCs develop a clear anisotropic shape. The breadth of the chains formed is not that much larger than the cross sectional diameter of the NCs observed in Fe065 [Fig. 1(a)], but their lengths are significantly greater as is observed in Fe130 [Fig. 1(c)]. Additionally, the size distribution becomes broader with increasing $[\text{Fe}]$.

Magnetization measurements, $M(H)$, were made on all samples in the temperature range 2–300 K and some representative hysteresis loops, corrected for the diamagnetic contribution of the Si substrates, are shown in Fig. 3. The loop shape measured for FE065, that consists of NCs of quasi-circular cross section, varies greatly with temperature [Fig. 3(a)], while its high field (1.5–2 T) magnetization value is significantly reduced as the temperature is increased. Quantitatively, similar behavior was found for FE095, which also contains isolated NCs although they are elongated in shape. In contrast, the loop shape and high field magnetization value of samples with quasicontinuous Fe layers vary little with temperature, as shown in Fig. 3(b) for FE145. The value of magnetization per Fe atom, measured at 10 K in a magnetic field of 2 T, is plotted as a function of $[\text{Fe}]$ in Fig. 4. It is found to increase from $1.4 \mu_B/\text{Fe atom}$ for the sample with lowest $[\text{Fe}]$ (FE065), and tends toward saturation at a value of $2.2 \mu_B/\text{Fe atom}$ for samples with quasicontinuous Fe layers, the latter being the expected value for α -Fe. The temperature dependence of the magnetization of the two samples containing isolated NCs ($[\text{Fe}] \leq 9.5 \times 10^{15} \text{ atoms/cm}^2$), measured for increasing temperature in a field of 5 mT,

FIG. 3. Hysteresis loops of (a) FE065 and (b) FE145 measured at various temperatures.

are shown in Fig. 5. Both ZFC and FC, in a field of 5 mT, data are shown. The ZFC magnetization curves increase with increasing temperature to reach a maximum at a blocking temperature, $T_B = 25$ K and 55 K for FE065 and FE095, respectively. The measuring field dependence of T_B for FE065 is shown in the inset of Fig. 5. A quasi-linear decrease of T_B is observed for increasing magnetic fields from $T_B \approx 23$ K at 1 mT to $T_B \approx 17$ K for an applied field of 30 mT.

Finally, the temperature dependence of the coercivity is shown in Fig. 6 for samples with different Fe morphologies ranging from small quasi-circular Fe NCs ($[\text{Fe}] = 6.5 \times 10^{15} \text{ atoms/cm}^2$) up to quasicontinuous Fe layers ($[\text{Fe}]$

FIG. 4. Value of magnetization per Fe atom measured in a field of 2 T at 10 K as a function of $[\text{Fe}]$. The horizontal dashed line corresponds to the expected value for α -Fe, whereas the vertical dashed line qualitatively indicates the critical $[\text{Fe}]$ at which quasicontinuous layers are formed.

FIG. 5. Temperature dependence of the FC (x) and ZFC (o) magnetization of (i) FE065 and (ii) FE095, measured in a magnetic field of 5 mT (field cooling carried out under same field). The inset shows the measuring field dependence of the blocking temperature of FE065.

$= 24.5 \times 10^{15}$ atoms/cm²). Samples containing isolated NCs have high coercivity at very low temperature ($T < 10$ K), but the coercivity drops rapidly to zero as the temperature is increased, whereas samples containing quasicontinuous Fe layers ($[\text{Fe}] \geq 14.5 \times 10^{15}$ atoms/cm²) have very low coercivity values over the whole temperature range studied.

IV. ANALYSIS AND DISCUSSION

The use of PLD in a vacuum allows the synthesis of well isolated and homogeneously distributed NCs when the metal content per layer is below a critical value as shown in Fig. 1(a). The nucleation of metallic NCs on an oxide surface, as reported in the present work, is related to the Volmer–Weber growth mode, which occurs for most metals grown on oxide surfaces, involving the formation of isolated three-dimensional (3D) islands on the substrate.^{20,24,28} In the present case, the nucleation sites at the substrate are related to Fe atoms reaching the substrate during the first laser pulses. They are randomly distributed on the surface and this fact, together with the high mobility of the atoms arriving at later pulses, favors the formation of an in-plane homogeneous distribution of NCs. The images shown in Fig. 1 only provide information about the in-plane dimensions of the NCs. Nevertheless, in a previous work, it has been shown that for NCs of a small circular cross section, similar to those

shown in Fig. 1(a), the out-of-plane dimension is close to the in-plane diameter.²⁴ Thus, in this case, the NCs can be considered quasi-spherical as a first approximation. If the Fe content per layer is further increased, coalescence and aggregation lead to the formation of elongated NCs [Fig. 1(b)] and then, long metal chains for even higher metal contents as observed in Fig. 1(c) and Fig. 2, which show a small increase of the nanocrystal breadth, but a significant increase in their length.

The magnetic behavior of these nanocomposite films is found to change as the Fe content per layer is increased, as shown in the representative comparison made in Fig. 3 between FE065, which contains quasi-spherical NCs, and FE145, which contains quasicontinuous Fe layers. Thus, magnetization measurements may be used to compliment the structural characterization of such systems. While the $M(H)$ loops of the samples containing quasicontinuous Fe layers maintain their ferromagnetic character over the temperature range studied [Fig. 3(b)], the observed change with temperature in the magnetization loops of samples containing isolated NCs [Fig. 3(a)], i.e., the significant decrease in the saturation magnetization and the strong decrease in initial susceptibility, is characteristic of a crossover from a ferromagnetic to a superparamagnetic regime. Such a crossover occurs when the thermal energy $k_B T$ becomes comparable with the magnetic anisotropy energy so that thermal fluctuations in the orientation of the magnetic moments average out the magnetization and thus effectively destroy the ferromagnetism on the measurement timescale. The relaxation of magnetization for a single particle, across an energy barrier ΔE in a reverse magnetic field of induction B , is characterized by a relaxation time τ given by

$$\tau^{-1} = f_0 \exp[-\Delta E(B)/k_B T], \quad (1)$$

where f_0 is an attempt frequency usually taken to be 10^9 – 10^{11} Hz,²⁹ k_B is Boltzmann's constant, and T is the particle temperature. For Stoner–Wohlfarth coherent rotation and considering that the particles are randomly oriented,³⁰ we have

$$\Delta E(B) \propto K_{\text{eff}} V (1 - B/B_0)^{3/2}, \quad (2)$$

where K_{eff} is the effective anisotropy per unit volume, V is the volume of the particle, and B_0 is the value of external reverse magnetic induction which eliminates the energy barrier to magnetization reversal. The blocking temperature, T_B , is the temperature at which the energy barrier is comparable to the thermal energy $k_B T$, so that for measurements made on a time scale of 1 s under a reverse field of induction B , Eq. (1) gives

$$25 k_B T_B(B) \approx \Delta E(B), \quad (3)$$

and the extrapolated zero-field value of $T_B(0)$ can be expressed as

$$25 k_B T_B(0) \approx K_{\text{eff}} V. \quad (4)$$

T_B can be estimated by measuring the temperature dependence of magnetization, under various values of applied field, for increasing temperature after FC and ZFC. The low temperature peak in the ZFC magnetization curve, measured

FIG. 6. Temperature dependence of coercivity for samples with varying $[\text{Fe}]$.

under a field of 5 mT, occurs at 25 K and 55 K for FE065 and FE095, respectively (Fig. 5). The lower T_B value for the sample with the lowest [Fe] reflects the fact that the NCs in this sample are smaller while the narrower magnetization peak width of this sample reflects the more homogeneous NC size and shape distribution. A linear extrapolation of the data shown in the inset of Fig. 5 (blocking temperature versus measuring field) to zero field gives $T_B(0) \approx 23$ K for the sample with lowest [Fe] on the time scale of our measurement (≈ 1 s). If we consider this value of T_B and assuming an average particle volume of 5.6 nm^3 (based on HRTEM analysis from which we have $d_{av} = 2.2 \text{ nm}$), we can deduce a $K_{eff} \approx 1.4 \times 10^6 \text{ J/m}^3$ from Eq. (4). α -Fe has a cubic crystal structure with equivalent directions of easy magnetization along the three four-fold axes of the cubic structure. Thus, the estimated value of K_{eff} should be compared with $K_1(\alpha\text{-Fe})/4 = 1.25 \times 10^4 \text{ J/m}^3$. The fact that K_{eff} is two orders of magnitude greater than the bulk magnetocrystalline anisotropy constant of α -Fe suggests that there are strong surface contributions to anisotropy in these Fe NCs.^{5,20,31} Shape anisotropy should also be considered as these particles are probably slightly flattened rather than truly spherical. The maximum value of shape anisotropy, which corresponds to the case of an infinite thin film, is given by $1/2\mu_0 M^2$ and assuming the saturation magnetization value of α -Fe this amounts to $1.6 \times 10^6 \text{ J/m}^3$. Though this value is almost equal to the estimated value of anisotropy, the shape of the Fe NCs is far from thin-film form so shape anisotropy alone can not account for the observed effect.

The sample containing the lowest [Fe], FE065, was chosen as a model system for further analysis because it contains well isolated Fe NCs of homogeneous quasi-spherical shape and narrow size distribution. In this case, the magnetization curves in the superparamagnetic regime can be analyzed within the framework of the Langevin theory of paramagnetism. The magnetization of a (super)paramagnetic particle can be expressed as:

$$\mathbf{m} = m_0 \mathbf{L}(x) = m_0 \{\coth(x) - 1/x\}, \quad (6)$$

where $\mathbf{m}_0$ is the particle moment at temperature T , $\mathbf{L}$ is the Langevin function, and $x = m_0 \mu_0 H / k_B T$. The magnetization of a sample consisting of N noninteracting NCs is given by:

$$\mathbf{M} = N m_0 \{\coth(x) - 1/x\}, \quad (7)$$

and a universal curve of M/m_0 versus $m_0 \mu_0 H / k_B T$ is expected for all temperatures. Fitting of magnetization curves in the superparamagnetic regime can be used to estimate the number of NCs and the average magnetic moment per NC. The as-measured 150 K magnetization curve (in which magnetization is expressed per unit surface area of sample, $\mathbf{M}_{ua}$) was fitted with a two term (superparamagnetic and diamagnetic), three parameter (N_0 , m_0 , and χ_{Si}) equation:

$$\mathbf{M}_{ua} = N_0 m_0 \{\coth(x) - 1/x\} + \chi_{Si} \mu_0 \mathbf{H}, \quad (8)$$

where N_0 is the number of NCs per unit area and χ_{Si} is the diamagnetic susceptibility of Si. The second term was added to account for the contribution of the Si substrate. This fit gives a value of $\chi_{Si} = -2.6 \times 10^{-4} \text{ emu/T/cm}^2$, which is comparable to the value of $-2.2 \times 10^{-4} \text{ emu/T/cm}^2$ mea-

FIG. 7. Sample magnetization divided by NC moment (M/m_0) plotted as a function of $m_0 \mu_0 H / k_B T$ for FE065, measured at 150, 200, 250, and 300 K.

sured on a reference Si substrate. The value of N_0 thus estimated is $2.37 \times 10^{13} \text{ NCs/cm}^2$. N_0 and χ_{Si} should be constant for all temperatures, and indeed using the values obtained at 150 K, the higher temperature curves (200, 250, and 300 K) could be fitted with just one variable, m_0 . Using these values of m_0 , it is possible to plot M/m_0 versus $m_0 \mu_0 H / k_B T$ (Fig. 7). The fact that a universal curve is found, verifies that the NCs are superparamagnetic and validates the use of this method to estimate N_0 . Dividing the number of NCs per unit area by the number of Fe atoms per unit area (as estimated from RBS), we can estimate that, on average, there are 1350 Fe atoms per NC in FE065.

From the plot of the 10 K values of magnetization, measured in a field of 2 T, as a function of [Fe] (Fig. 4), we see that while the samples containing quasi-continuous layers of Fe have the saturation magnetization value expected for α -Fe ($2.2 \mu_B/\text{Fe atom}$), the samples containing isolated Fe NCs have significantly lower values. The fact that the reduction in the value of magnetization per Fe atom increases as the surface to volume ratio increases indicates that this could be related either to a surface effect or to a finite size effect.²⁰ Similar results for a comparable system of Fe NCs in an Al_2O_3 host prepared by sputtering, i.e., extrapolated 0 K values of saturation magnetization reaching 60–70% that of α -Fe, were attributed to spin canting on the surface of the Fe NCs,³² an effect known to happen in fine Fe-oxide particles.³³ However, contrary to oxides in which superexchange interactions are known to depend strongly on 3d ion-O-3d ion bonding angles, exchange interactions in ferromagnetic 3d metals should prevent any significant deviations of the surface magnetic moments and indeed Mössbauer studies indicate that surface spins remain in a saturated state on the surface of very fine metallic Fe particles.³⁴ We thus suggest that the observed effect is due to the formation of an oxide layer on the NC surface leading to a core shell structure (core of α -Fe + shell of Fe-oxide). Knowing the average number of Fe atoms per NC (≈ 1350) and the average moment per Fe atom ($\approx 1.4 \mu_B/\text{Fe atom}$), and supposing that the measured magnetization is coming from the core assumed to be formed of α -Fe atoms with a moment of $2.2 \mu_B$, we can estimate that 65%, i.e., 870 Fe atoms, occupy the core while the remaining 480 Fe atoms are located

in a surface layer which is assumed to be paramagnetic or antiferromagnetic. Taking the density of α -Fe (7.87 g/cm^3), an average oxide density (5.47 g/cm^3 —average over FeO , Fe_2O_3 , and Fe_3O_4) and an average oxide Fe content (73.3 wt %), this corresponds to 10.3 nm^3 of α -Fe and 11.1 nm^3 of oxide. For a spherical NC, this corresponds to an α -Fe core of diameter 2.7 nm and an oxide shell of thickness 0.4 nm. This estimate of the size of the metallic Fe core agrees reasonably with that determined from HRTEM analysis ($d_{\text{av}} = 2.2 \text{ nm}$). The thinness of the proposed oxide layer suggests a limited source of oxygen. Two possible explanations exist for the oxidation of the Fe NCs. Either the presence of residual O_2 in the deposition chamber, which has been proposed as a source of oxidation of Fe NCs for vacuum pressures similar to those used in the present work,³⁵ or the presence of oxygen in the matrix in which the NCs are embedded. The low amount of O_2 and / or the high oxygen affinity of Al limits the oxidation of the Fe NCs, leading to the formation of a thin oxide layer surrounding a metallic core. The latter reasoning is supported by the fact that annealing of $\text{Fe/Al}_2\text{O}_3/\text{Fe}$ tunnel magnetoresistance junctions leads to an improvement in the quality of the Fe layers.³⁶

The particle size dependence of coercivity that can be deduced from Fig. 6, (i.e., the significant increase in coercivity with particle size reduction at low temperature) is qualitatively similar to that reported for systems of oxygen surface passivated Fe NCs prepared by evaporation techniques.^{35,37} Gangopadhyay *et al.* attributed the relatively high coercivity of their smallest NCs, similar to those produced in this work, to magnetic interactions at the core-shell interface.³⁵ Del Bianco *et al.* studied a sample consisting of core-shell structured Fe-FeO_x NCs with diameters in the range 15–40 nm having an oxide surface thickness of about 2 nm.³⁷ They found that low temperature (5 K) magnetization loops measured after FC (2 T) were nonsymmetric, having higher coercivities in the field direction opposite to that in which the sample was cooled. They attributed this behavior to exchange coupling between the ferromagnetic α -Fe core and the oxide shell having a spin-glass structure with a freezing temperature of about 50 K and proposed that these exchange interactions were responsible for the high coercivities of the smallest particles. To check for exchange coupling between the α -Fe core and the FeO_x shell of our smallest NCs, we measured hysteresis loops at 2.5 K after cooling in a field of 2 T but no field bias was observed (data not shown). In fact, this is quite reasonable as the oxide layer is so thin, that only the surface layer of Fe atoms should belong to the oxide and the oxide is therefore unlikely to influence magnetization reversal in the core. Indeed, it is known that the exchange biasing of a ferromagnetic layer by an antiferromagnetic one decreases as the thickness of the antiferromagnetic layer decreases.³⁸ Thus, we tentatively ascribe the large low temperature values of coercivity in our samples with the smallest Fe NCs not to exchange interactions but to a strong surface contribution to anisotropy, that is also responsible for the enhancement of K_{eff} as shown, which becomes significant for very small NC sizes.

The temperature dependence of coercivity (Fig. 6) is also qualitatively similar to the results of Gangopadhyay and

Del Bianco.^{35,37} Gangopadhyay *et al.* attributed the rapid drop in coercivity with increasing temperature in their samples of smallest particle size to the quenching of the core-shell interactions upon the transition to the superparamagnetic state of the oxide surface.³⁵ Similarly Del Bianco *et al.* invoked the quenching of core-shell interactions above the spin-glass transition temperature of the oxide shell, but the superparamagnetic behavior of the α -Fe cores of the finest particles was also acknowledged to influence the temperature dependence of coercivity.³⁷ Additional analysis indicates that the rapid drop to zero of coercivity as temperature is increased in our samples of smallest NC size is due to thermal activation (i.e., superparamagnetic behavior) of the α -Fe cores which have a relatively narrow size distribution.³⁹ The much weaker temperature dependence of coercivity in the samples with quasicontinuous Fe layers is due to the fact that thermal effects are much less important and the temperature dependence of coercivity should vary as the temperature dependence of magnetocrystalline anisotropy.

V. CONCLUSIONS

Sequential PLD has been used to prepare nanocomposite $\text{Fe:Al}_2\text{O}_3$ thin films. The morphology of the Fe layer was varied from quasi-spherical NCs to quasicontinuous layers by increasing the number of laser pulses on the Fe target. The evolution in the shape and size of the Fe layer is reflected in magnetic measurements. While the samples containing quasicontinuous Fe layers were ferromagnetic at all temperatures measured, a crossover from a ferromagnetic to a superparamagnetic regime was evidenced in the samples containing small isolated NCs. FC/ZFC measurements were used to measure the blocking temperature of samples with low [Fe] in various fields and a zero-field blocking temperature of 23 K was extrapolated for the sample of lowest [Fe], which contained a homogeneous distribution of quasi-spherical NCs with an average diameter of 2.2 nm. Taking the average NC size from HRTEM images of this sample, this corresponds to an effective magnetic anisotropy of $1.4 \times 10^6 \text{ J/m}^3$. Analysis of the high temperature magnetization loops of this sample ($>150 \text{ K}$) within the framework of the Langevin theory of paramagnetism together with RBS data was used to estimate the average number of Fe atoms in each NC (1350 atoms). The moment per Fe atom in the samples with low [Fe] is reduced with respect to the value for α -Fe ($2.2 \mu_B/\text{atom}$) and we attribute this behavior to the presence of a thin Fe-oxide surface shell. From these results, we have estimated an α -Fe core diameter of 2.7 nm and an oxide layer thickness of 0.4 nm, the former agreeing reasonably well with HRTEM estimates. The relatively large low temperature values of coercivity in the samples with low [Fe] are attributed to a strong surface contribution to anisotropy while the temperature dependence of coercivity in these samples is attributed to thermal activation.

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