Interplay between particle anisotropy and exchange interaction in Fe nanoparticle films

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The magnetic properties of Fe nanoparticles films were investigated by magnetization measurements and Monte Carlo simulations. The films were produced by femtosecond pulsed laser deposition assisted by irradiation of nanoparticles with a nanosecond UV laser pulse, appropriately delayed, during their flight from the target to the substrate. The films consist of nanoparticles with a disklike shape. The initial magnetization curve exhibits a stepwise behavior, characterized by a reversible plateau followed by rapid irreversible increments. The observed behavior, induced by the peculiar nanoparticle film morphology, is the result of the competition between particle anisotropy, dipole-dipole interactions, and interparticle exchange coupling. This picture is supported by Monte Carlo simulations, satisfactorily reproducing the experimental observations.

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I. INTRODUCTION

The macroscopic behavior of a disordered assembly of nanoparticles (NPs), with randomly oriented magnetic moments, strongly depends on the size, shape, and topology of the NPs, and the type and strength of their magnetic coupling.[1] In the presence of extended and strong enough interparticle interactions a collective magnetic state is established, with a variety of possible magnetic configurations, resulting from a number of competing energy terms.[2] A deeper understanding of these interactions is necessary to clarify the physics of these systems and their use in the development of high-performance magnetic materials.[3] The individual particle anisotropy energy competes with the interparticle exchange energy in determining the orientation of the particle magnetic moments. In particular, according to the random-anisotropy model,[4] if $D_a < \delta_0$, where D_a is the average diameter and $\delta_0[=(A/K)^{1/2}]$ is the bulk ferromagnetic exchange length (A and K being the exchange and anisotropy constants), the ferromagnetic correlation length extends over several particles. On the other hand, if $D_a \gg \delta_0$, the individual particle anisotropy energy predominates.

In this paper, we report on the investigation of the magnetic properties of Fe NP films, where $D_a < \delta_0$.

The observed magnetic behavior is determined by the peculiar morphology of the films, induced by femtosecond pulsed laser deposition assisted by irradiation of nanoparticles with a nanosecond UV laser, appropriately delayed during their flight from the target to the substrate. The films consist of NPs with a disklike shape; the high aspect ratio and the very small particle size (most of them are smaller than 5 nm) induce a high particle anisotropy energy due to shape and surface contributions larger than the interparticle exchange energy. This is the opposite of what is expected in bulk iron and in the commonly investigated nanoparticle systems of 3d ferromagnetic elements and their alloys. In the investigated films, exchange interactions are reduced by the presence of voids between particles and disordered particle interfaces, with reduced atomic coordination with respect to the crystals.

The initial magnetization curve exhibits a stepwise behavior, characterized by a reversible plateau followed by rapid irreversible increments. Such behavior recalls magnetization steps observed in phase-separated manganites,[5] in intermetallic compounds,[6] in metamagnets,[7] in clean metals,[8] and in molecular magnets,[9] but in such systems the steps have a different physical explanation. The stepwise behavior exhibited by our films is unusual for a disordered assembly of nanoparticles. Such behavior, well reproduced by Monte Carlo simulations, is interpreted as the result of competing high particle anisotropy, dipole-dipole interactions, and interparticle exchange coupling.

II. RESULTS AND DISCUSSION

A. Film deposition and morphological characterization

Fe NP films were deposited by femtosecond laser ablation[10] and collected on a substrate, as described in Ref. 11. Exploiting the technique presented in Ref. 12, the films' deposition was assisted by irradiation of the ablated NPs, in flight prior to deposition, with an appropriately delayed nanosecond UV laser beam. The main effect of the UV beam irradiation was the reduction of the NP average size by surface vaporization of NPs in the ablated plume.[12] The films deposited with this method will be referred to as fsPLD+UV films.

The NP size distribution was determined by atomic force microscopy (AFM) analysis of a deposit less than one layer onto mica substrates. A typical AFM image is reported in Fig. 1. The analysis was performed by a Nanoscope V atomic force microscope (Veeco Instrument Inc. Santa Barbara Ca, USA) operating in *tapping mode* (scan size and rate of 2 μm and 1 Hz, respectively), equipped with a silicon tip having a nominal curvature radius of about 2 nm. The subsequent data analysis was performed by using SPIP image analysis software (Image Metrology, DK). After performing deconvolution on each AFM image in order to avoid the tip size effect, the average particle size in the planes parallel and orthogonal to the substrate was evaluated. In this way, the three-dimensional view of the deposits was reconstructed.

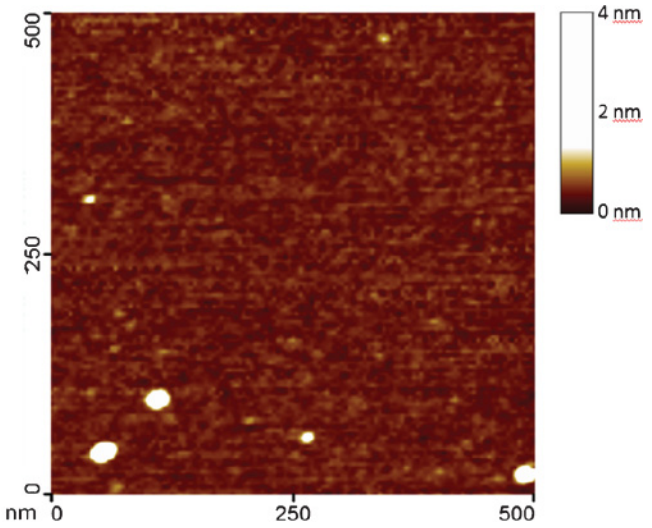

FIG. 1. (Color online) Typical AFM image of deposits less than one layer.

As shown in Fig. 2, most particles (90%) have an in-plane diameter D smaller than 10 nm and among these the largest fraction is smaller than 5 nm. There is no peak in this small particle size distribution, but rather a continuous increase in the number of particles as their size is reduced. This result, similar to that observed by Cebollada *et al.*,[13] is consistent with theoretical calculations that describe the ablation process as the emission of particles with a wide range of sizes down to atomic ones.[14] The median height of these small particle is $d_m = 0.6$ nm. They have a disklike shape with a median aspect ratio $(D/d)_m = 8.0$. As far as the very few larger particles are concerned, their in-plane diameter is mainly between 10 and 60 nm as shown in the inset of figure Fig. 2(a).

The main effect of the UV irradiation has been a decrease of both the NP average size and its dispersion, as well as an increase in their flatness, in comparison with the standard fsPLD (single irradiation),[11] which in the same experimental conditions has produced particles with a median D value $D_m = 19.0$ nm, a median height value $d_m = 3.0$ nm, and a median aspect ratio $(D/d)_m = 6.0$.

NP-assembled fsPLD+UV films about 5 nm thick were obtained after 60 min of deposition. The size of the Fe NPs in the films is fairly similar to that measured in deposits of less than one layer, indicating that there is no significant coalescence among the particles. The actual concentration of particles in the film is about 50% due to the presence of some voids between them.

The smaller NPs are exchange-coupled and form a carpet-like structure. The few larger NPs (>10 nm) are well separated from each other and then weakly interact between them.

For the bigger particles, x-ray diffraction (XRD) shows a body-centered cubic structure with a lattice spacing of 0.286 nm, without any evidence of traces of oxides. However, some oxidation of the particles at the film surface, not detectable by x ray, is expected, although the films were prepared in high-vacuum conditions and the magnetic measurements were performed in a helium atmosphere just after they were removed from the deposition chamber. In order to detect the

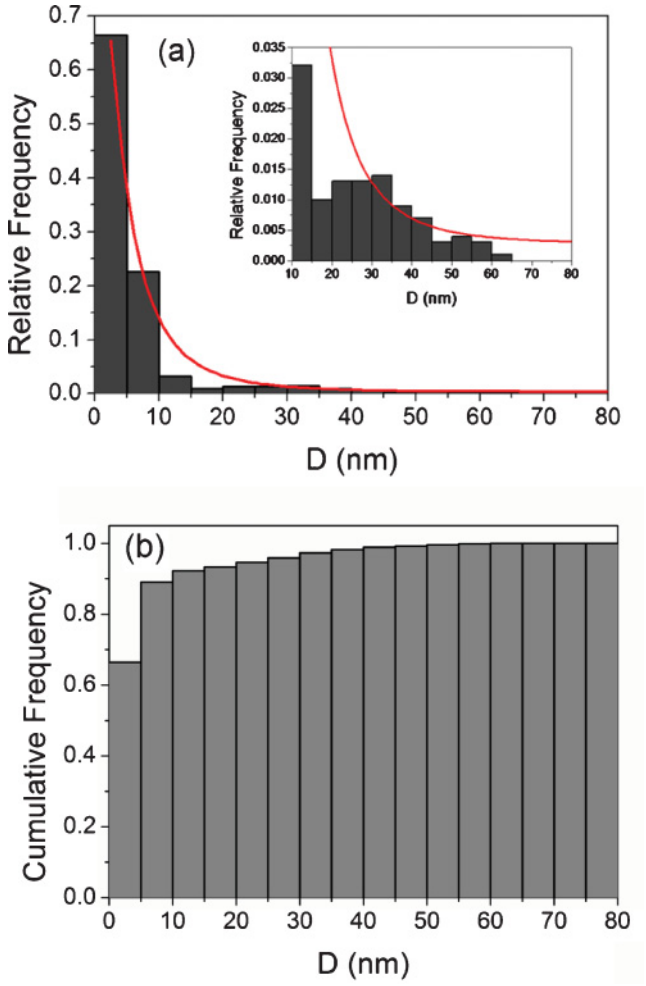

FIG. 2. (Color online) (a) Size distribution of the NP in-plane diameter D. The inset shows the magnification of the region of big particles. (b) Cumulative distribution of the in-plane diameter.

presence of possible antiferromagnetic (FeO, α-Fe_2O_3) or ferrimagnetic (γ-Fe_2O_3, Fe_3O_4) oxide phases with a larger anisotropy of Fe particles, we measured the hysteresis loop at 5 K after field cooling from high temperature. Their presence should produce a shift of the hysteresis loop due to the exchange coupling at the interface with the Fe particles (exchange bias effect).[15] No shift was observed, suggesting that surface oxidation is scarce and that the oxide shell is magnetically disordered.

B. Magnetization measurements

In-plane magnetization measurements were performed, after accurate ac demagnetization, by a vibrating sample magnetometer. Figure 3 reports a typical hysteresis loop of the Fe NP films at RT. The initial magnetization curve shows a stepwise behavior, quite unusual for a disordered assembly of nanoparticles, although expected in some amorphous systems.[16]

The following different regions can be distinguished by increasing the magnetic field: (1) a low-field region of almost zero susceptibility from zero up to $H_1 = 3500$ A/m, perfectly reversible; (2) a big jump (irreversible as shown by minor

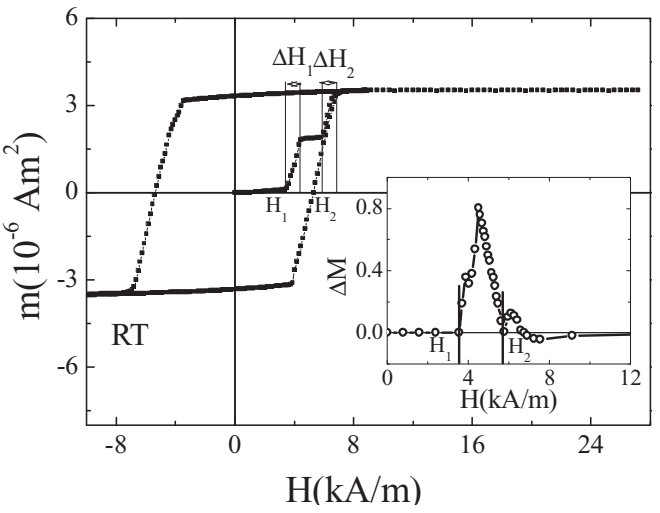

FIG. 3. Initial magnetization curve and hysteresis loop for Fe NP films at RT. The inset shows $\Delta M(H)$ behavior of the fsPLD+UV NP-assembled Fe samples.

loops), occurring in a narrow field interval $\Delta H_1 \approx 900$ A/m; (3) a second region of almost constant magnetization, characterized by reversibility that extends up to $H_2 = 5900$ A/m; (4) a second irreversible jump, occurring in a field interval $\Delta H_2 \approx \Delta H_1$; (5) a final approach to saturation starting from $H = 7000$ A/m. The same qualitative behavior was found in different films with small changes in the values of the jump fields as well as in the width of the plateau.

In the inset of Fig. 3, the result of the analysis of the field dependence of the remanent magnetization curves is reported according to the relationship[17]

$$\Delta M(H) = \{M_D(H) - [M_R(\infty) - 2M_R(H)]\}/M_R(\infty), \quad (1)$$

where $M_R(\infty)$ is the saturated remanence, $M_R(H)$ is the isothermal remanent magnetization, measured starting from an initially ac-demagnetized sample, and $M_D(H)$ is the dc-demagnetization remanent magnetization, measured starting from a previously saturated state and then applying increasing values of reverse field. Two distinct positive peaks are observed: a stronger and a weaker one at a field just above H_1 and H_2, respectively, corresponding to the irreversible increments in the initial magnetization curve. The positive value of $\Delta M(H)$ and the high remanence ratio ($M_R/Ms \geqslant 0.9$) suggest that exchange coupling is the dominant interparticle interaction.[18] Indeed, according to the Stoner-Wohlfarth model, $\Delta M(H) = 0$ in the absence of interparticle interactions; positive values are predicted for exchange interactions promoting the magnetized state, whereas negative values are predicted for dipole-dipole interactions.

The first plateau in the initial magnetization curve and the absence of irreversible processes at low-field values are unexpected in the frame of the random anisotropy model. Indeed, this indicates that interparticle exchange interactions are frustrated, although in the investigated sample, where $D_m < \delta_0$ is the in-plane particle median diameter, most particles (90%) are smaller than the bulk ferromagnetic exchange length in iron (23 nm).[19] This suggests that the very small size and the peculiar particle morphology produced by fsPLD+UV, i.e., the high aspect ratio of nanoparticles, strongly enhancing the surface and shape particle anisotropy, play a dominant role in determining the magnetic properties of the material. The possibility that the observed stepwise behavior is due to the coexistence of two phases with different magnetic anisotropy or to a bimodal particle size distribution is excluded, as the structural and morphological analysis does not provide any indication of them.

The observed plateau below H_1 should originate mainly from the competition between individual particle anisotropy, tending to orient the particle moments along their easy axes, and interparticle exchange coupling, within particle clusters, tending to align the particle moments. Moreover, the random local fields produced by the bigger particles and the dipolar interactions between them (randomly distributed due to the distribution of interparticle distances) would also compete with interparticle exchange interactions. On the other hand, the presence of a probable nonstoichiometric and disordered oxide shell for particles at the film surface should reduce the possibility of interparticle exchange interactions.

The resulting cluster moment is expected to be very low and randomly oriented, as in a cluster glass-type system. The particle system behaves as a system with a quite high actual anisotropy and then does not respond to the magnetic field until the field reaches the H_1 value, at which point the particle anisotropy is overcome and then the particle moment's alignment along the anisotropy axes is broken. Thus, exchange coupling prevails in competition with particle anisotropy, aligning the particle moments within the clusters and then determining the rapid increase of the magnetization when the field H_1 is applied. The effect of the magnetic field on this competition favors the ferromagnetic coupling between particles.

A second plateau is observed between ≈ 4400 A/m and H_2, revealing the presence of another frustrated state. The second plateau should be the result of the competition which is established between the particle clusters anisotropy and the intercluster exchange interaction. Actually, a cluster of exchange-coupled particles behaves as a big single-domain ferromagnetic particle with the anisotropy energy density larger than the intercluster exchange energy density. At the field H_2, such anisotropy is overcome; the intercluster interaction prevails, leading to the growth of the cluster size with increasing field, and then there is a further increase in the magnetization toward the saturation.

In order to provide further evidence of the observed peculiar magnetization process and to support the proposed explanation, the behavior of the first magnetization curve was also investigated at low temperature (Fig. 4).

At 10 K, the steps occur at larger fields. This is coherent with the need of larger fields to overcome the anisotropy, due to the increase of anisotropy and then the decrease of δ_0 with decreasing temperature.

A third step is observed, reflecting the existence of a further state of frustrated exchange interactions, related to the anisotropy, with respect to room temperature. Such a further step would exclude the possibility that the stepwise behavior is caused by the coexistence of two phases with

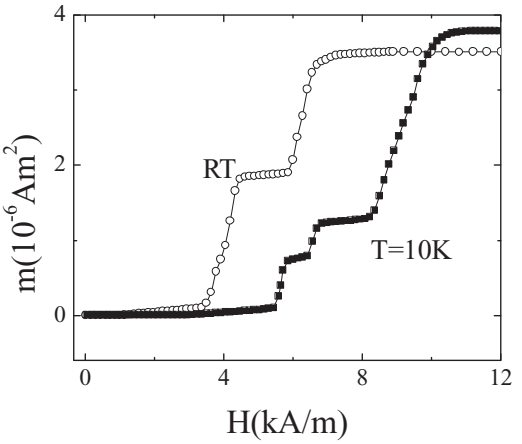

FIG. 4. Comparison of initial magnetization curves at RT and 10 K, in Fe NP films.

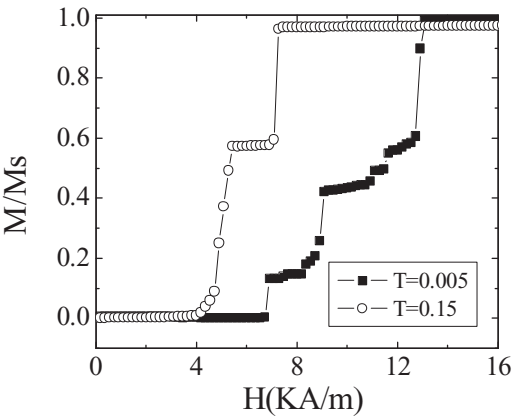

FIG. 5. Initial magnetization curves at RT ($T = 0.15$ in the model) and 1/30 RT ($T = 0.005$), as obtained by MC simulations.

different magnetic anisotropy or by a bimodal particle size distribution.

The proposed interpretation is coherent with the model proposed by Löffler *et al.*[20] According to them, the interparticle exchange can be considerably weaker than intraparticle exchange and, for $D_a < \delta_0$, the random-anisotropy model applies as long as $ID_a/Aw \geqslant 1$, where I (> 0) represents the random ferromagnetic exchange across the interfaces of width w. On the other hand, for $ID_a/\mathrm{w} < KD_a{}^2 < A$, the particles can behave as randomly coupled large spins, with spin-glass properties in three dimensions.[21]

Due to the disklike shape of our particles, generated by fsPLD+UV, both $(D/d)_m$ and the surface-to-volume ratio of the nanoparticles are very large. According to the model developed by Bødker *et al.*,[22] the effective anisotropy constant in our system is larger than that expected for conventional nanogranular films where particles are spheroidal.

With respect to a compact NP system, the interparticle exchange coupling and the interaction between clusters of NPs are significantly reduced because of the presence of voids and disordered oxide shell for particles at the film surface. This fact, together with the very large particle anisotropy, can explain the experimental evidence of frustration of exchange interactions, despite the condition $D < \delta_0$ for about 90% of nanoparticles in the investigated films.

C. Monte Carlo simulations

In order to further support the proposed interpretation, the first magnetization curve was modeled by the Monte Carlo (MC) technique using the standard Metropolis algorithm.[23] Using input from the AFM images, the following model has been developed: (i) the nanoparticles form small clusters of few particles in contact and the few big particles are well separated from each other; the mean particle concentration is 0.5; (ii) the values of interparticle exchange coupling (J) and particle anisotropy energy (k) are competing; the ratio J/k is taken equal to 1; (iii) the exchange interaction between big particles is negligible; (iv) small long-range dipolar interparticle interactions on the order of $g/k = 0.12$ are considered in the whole system. The results of the simulations for two temperatures are shown in Fig. 5. As seen from this figure, the numerical model confirms the experimental findings reproducing the stepwise behavior of the virgin magnetization curves and the increase of the number of steps with decreasing temperature.

III. CONCLUSIONS

In conclusion, we have observed an unusual stepwise behavior of the virgin magnetization curve in a Fe nanoparticle film, produced by fsPLD assisted with a secondary UV irradiation. The stepwise behavior is attributed to the competition between the high particle surface and shape anisotropy, induced by the film deposition method, and interparticle exchange interactions within the particle cluster. This, together with the effects of random dipolar interactions and of the presence of some voids between the particles and probable disordered oxide shells at the film surface, produces a frustration of exchange interactions both in the demagnetized state and at intermediate stages of the first magnetization process, although the NPs' median size is much lower than the bulk ferromagnetic exchange length. The observed behavior is well reproduced by Monte Carlo simulations accounting for competing values of particle anisotropy energy and interparticle exchange-coupling energy.

The observed process is attractive in view of developing methods for tailoring the equilibrium conditions between individual particle anisotropy and interparticle exchange interaction in magnetic NP systems in order to optimize the performance of magnetic devices.

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