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Role of Dipolar Interactions and Volume Particle Size Distribution on the Nonmonotonic Magnetic Field Dependence of the Blocking Temperature in Magnetic Nanoparticles

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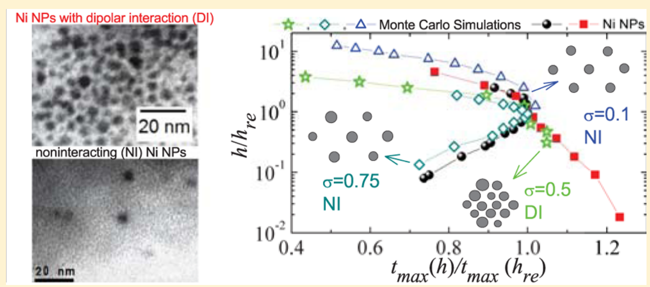
ABSTRACT: The nonmonotonic behavior of the magnetic field dependence H of the superparamagnetic blocking temperature $T_B(H)$ (or $T_{max}(H)$) of an assembly of magnetic nanoparticles NPs was studied both experimentally and theoretically. We have combined the measurements of zero-field cooling ZFC magnetization curves under H performed on samples with increasing concentration of Ni nanoparticles and Monte Carlo simulations. As a result, we have found that increasing the strength of the dipolar interaction between granules and the occurrence of a very narrow width of a log-normal volume particle size distribution of the NPs suppress the nonmonotonic behavior of $T_{max}(H)$.



■ INTRODUCTION

The topic of magnetism in nanostructured materials has been attracting much attention due to the interesting features arising from the remarkable properties associated with finite size effects and their potential application in information storage, bioapplication, magnetic refrigeration, catalysis, and others.[1] Moreover, the understanding of their fundamental physical properties, particularly the dipolar interaction between nanoparticles, is of greatest importance for technological applications because it affects the magnetic properties of the system.

Assemblies of magnetic nanoparticles (NPs) display typical features of superparamagnetic (SPM) systems in a temperature window comprehended between T_{max} and the Curie (or Néel) temperature of the material. T_{max} is associated with a maximum in zero-field cooling (ZFC) magnetization $M(T,H)$ curves, a temperature close related to the blocking temperature (T_B) of the NPs system, which is given by[2]

$$T_B = \Delta E(H)/[k_B \ln(t_m/\tau_0)] \quad (1)$$

where $\Delta E = KV(1 - H/H_K)^{3/2}$ is the energy barrier,[3] K the uniaxial anisotropy constant, V the volume of the nanoparticle, H the applied magnetic field, H_K the anisotropy field, k_B the Boltzmann constant, t_m the measuring time, and τ_0 a constant of the order of 10^{-9}–10^{-12} s.

According to eq 1, T_B, which is close related to T_{max}, is magnetic field H dependent. Moreover, increasing in H is expected to shift T_{max} *monotonically toward lower temperatures*.[4] Such behavior has been observed theoretically[5] and experimentally.[6] However, an initial *increase* of T_{max} in the range of low H, leading to an *unusual, nonmonotonic field dependence of* T_{max}, has been also reported in several systems of diluted magnetic NPs.[7−11] In connection with the experimental results, different explanations have been offered to account for this interesting behavior, although its precise nature is still a matter of debate.[8−16]

We first mention that the unusual $T_{max}(H)$ dependence has been interpreted as a result of an apparent increase of the energy barrier $\Delta E(H)$ due to the spin reorientation of the NPs under the action of an applied magnetic field.[7] On the other hand, the initial increase of T_{max} at low H has been attributed to the resonant tunneling between pair of states on opposite sides of the anisotropy barrier,[10] a mechanism that was ruled out elsewhere.[16] Other authors have claimed that it is due to a nonlinear field dependence of the magnetization $M(T,H)$ of unblocked granules in systems with certain values σ of the width of a volume particle size distribution of NPs.[8,11,13,14] It has been also argued that the width of the barrier distribution increases slightly with increasing H, causing the observed initial increase of the average blocking temperature for low values of H.[9] In addition, from Monte Carlo simulations it was concluded that the nonmonotonic behavior was due to the strong surface magnetic anisotropy of the magnetic NPs.[15] Finally, by computing the contribution of dipolar interactions α to the longitudinal relaxation time, $T_{max}(H)$ was found to change from a bell-like to a monotonically decreasing function when the dipolar interaction between NPs increases.[12]

Irrespective of the origin of the nonmonotonic behavior of $T_{max}(H)$, it is always accompanied by a common feature of all the systems studied: the concentration of the magnetic material is rather low and actually below ~5 vol %.[7−11] Since the

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unusual $T_{max}(H)$ dependence has not been observed in specimens with high volume fraction of magnetic material, a precise control and understanding of the role played by dipolar interactions α in diluted systems of magnetic NPs is of paramount importance.

To gain insight into the unusual behavior of $T_{max}(H)$, we report here a systematic study of the ZFC magnetization curves taken under several H in a set of six *diluted samples* with varying Ni NPs content (x), or more appropriately, with different strength of dipolar interaction between NPs. Therefore, we have also performed Monte Carlo simulations of ZFC curves in systems of NPs in which the width of the volume particle size distribution σ and the dipolar interaction α between granules were systematically varied. Judging from the similarity of the results obtained both experimentally and theoretically, we argue that the occurrence of the nonmonotonic behavior in $T_{max}(H)$ is a result of the delicate balance between two contributions to the ZFC curves arising from (i) the width of the volume particle size distribution σ and (ii) the strength of the magnetic dipolar interaction α between NPs.

■ EXPERIMENTAL SECTION

Ni NPs samples, with increasing x, embedded in an amorphous SiO_2/C matrix were prepared through a method in which silicon oxyanions and the metal cation (Ni) are immobilized within a polymeric matrix based on polyester, as described in detail elsewhere.[17] All samples are composed of nearly spherical Ni NPs of ∼5 nm in diameter with a log-normal distribution of volume. The width of the volume particle size distribution σ was found to range from 0.7 to 0.9 for samples with x = 1.9, 2.7, 4.0, 7.9, and 12.8 wt % and σ = 1.3 for samples with x = 20.3 wt %. Values of σ were determined by the fittings of $M(H,T)$ curves in the SPM state by using the Langevin function, as described elsewhere.[18] The dipolar interactions in this set of samples were found to be negligible for the most diluted samples, with $x \leq 4.0$ wt %.[19] Furthermore, we have employed MC simulations to determine the ZFC(T,H) curves for an ensemble of NPs with different width of volume particle size distribution and strength of dipolar interactions. Measurements of dc magnetization $M(T,H)$ (or dc magnetic susceptibility $\chi(T)$) were performed in powder samples by using a Quantum Design SQUID magnetometer, in which curves were taken under ZFC conditions in a wide range of temperatures ($2 \leq T \leq 300$ K) and under several applied magnetic fields ($30 \leq H \leq 2000$ Oe). We have also measured the magnetic field dependence of the magnetization $M(H)$ in the temperature interval $2 \leq T \leq 350$ K under applied magnetic fields to ∓70 kOe.

■ MODEL AND SIMULATION

Monte Carlo simulations were carried out in a set of N = 2500 particles occupying the sites of a triangular lattice with lattice constant a. We assume the following model Hamiltonian for the system of interacting NPs:

$$\mathcal{H} = \frac{g}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\left[\frac{\vec{S}_i\cdot\vec{S}_j}{|\vec{r}_{ij}|^3} - \frac{3(\vec{S}_i\cdot\vec{r}_{ij})(\vec{S}_j\cdot\vec{r}_{ij})}{|\vec{r}_{ij}|^5}\right] - \sum_{i=1}^{N}K_i(\vec{S}_i\cdot\vec{e}_i)^2 - \sum_{i=1}^{N}\mu H S_{ix} \tag{2}$$

where the parameter $g = \mu_0\mu^2/4\pi a^3$, μ is the magnetic moment of the NPs, and $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$ is the distance between magnetic moments at the sites i and j. The magnetic moment of the ith particle is written as $\vec{\mu}_i = \mu\vec{S}_i$, where $\vec{S}_i$ is a unit vector, $|\vec{S}_i| = 1$, and an external magnetic field is applied along the x-direction. The unit vector $\vec{e}_i$ gives the direction of the easy axis of the ith particle. All the uniaxial axes are randomly distributed over the three-dimensional space, and K_i (= KV_i) represents the magnitude of the uniaxial anisotropy energy of the ith particle with volume V_i, that is chosen from a log-normal distribution given by

$$f(K_i) = \frac{1}{\sqrt{2\pi}K_i\sigma}\exp[-\ln^2(K_i/K_0)/2\sigma^2] \tag{3}$$

where σ is the width of the distribution and K_0 its median value. In our analysis, two dimensionless variables are defined: (i) $h = \mu H/K_0$, the reduced magnetic field, and (ii) $\alpha = g/K_0$, the relative strength of the dipolar interactions. We also measured the temperature of the system in reduced units $t = k_BT/K_0$.

The procedure we have used to determine the steady state of the system is based on the minimization of the free energy along with the Metropolis algorithm.[20] According to this algorithm, a magnetic moment of the system is selected at random, and we try to change its direction within a maximum solid angle that is temperature dependent.[21] Then, the change in the energy of the system (ΔE_{MC}) is calculated, and if $\Delta E_{MC} \leq 0$, the transition to the new configuration is accepted. Otherwise, if $\Delta E_{MC} > 0$, the transition to the new configuration is only accepted with probability $\exp(-\Delta E_{MC}/k_BT)$. The Monte Carlo step (MCs) is defined as the number N of trials to change the state of the system. For each value of temperature, we wait 10^4 MCs until the steady state of the system is attained. After this transient time, the component of the magnetic moment along the direction of the magnetic field over 10^3 time steps is recorded at each of 100 MCs and an average over 10^3 samples is performed.

We have also increased the temperature by Δt = 0.005, and the whole process is repeated for the new temperature, until a maximum temperature is reached. For each value of dipolar coupling $\alpha = g/K_0$, width σ, and magnetic field h, the ZFC curve is built by taking 40 different values of temperature. The median value of $K_0 = 1$ of the log-normal distribution for the uniaxial anisotropy energy was used in all curves. Each ZFC curve is then adjusted to a smooth function and from its maximum value T_{max} is defined. To determine a set of T_{max} values, ZFC curves for each pair of values of α and h were built. The samples are prepared, at low T, with an initial magnetization very close to zero. For each sample, a magnetic field is applied along the x-direction and the temperature is progressively raised. Furthermore, we have employed MC simulations to determine the ZFC(T,H) curves for an ensemble of NPs with different width of volume particle size distribution and strength of dipolar interactions.

■ RESULTS AND DISCUSSION

A succession of experimental ZFC curves under increasing H taken in the x = 4.0 wt % Ni sample with negligible dipolar interaction and σ = 0.76 is displayed in Figure 1. Two main features of these curves depend on the strength of the applied magnetic field: (i) the temperature T_{max} *decreases* with increasing H for $H > H_{re}$, as seen in Figure 1a, in agreement with the predictions of eq 1, and (ii) T_{max} *increases* with increasing magnetic field for $H < H_{re}$, as displayed in Figure 1b. The combined features of these ZFC curves results in the nonmonotonic behavior of $T_{max}(H)$ at the reentrant magnetic field (H_{re}), as displayed in Figure 1c, which is plotted in

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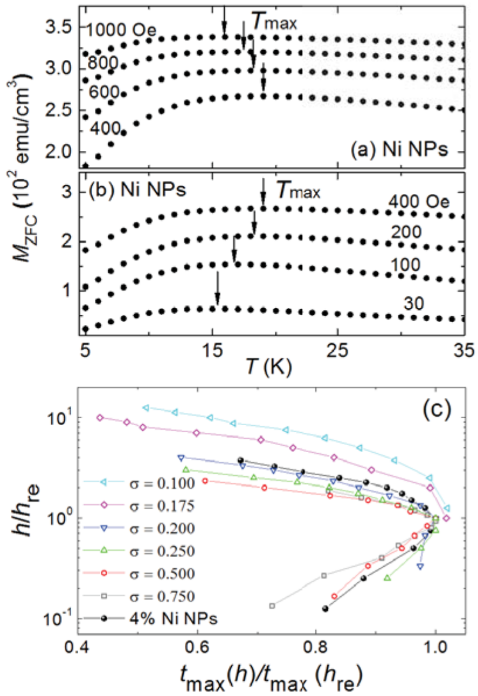

Figure 1. Expanded view of the low T region of ZFC curves for the sample $x = 4.0$ wt % Ni: (a) from 400 to 1000 Oe and (b) from 30 to 400 Oe. The arrows indicate the position of T_{max}. (c) Representation of the ratio h/h_{re} vs $t_{max}(h)/t_{max}(h_{re})$ for the sample $x = 4.0$ wt % (solid symbols) along with the results from MC simulation for a noninteracting system ($\alpha = 0$) with uniaxial anisotropy and volume log-normal distribution, for $\sigma = 0.100$, 0.175, 0.200, 0.250, 0.500, and 0.750 (open symbols). The solid lines are guides to the eyes.

normalized values [h/h_{re} vs $t_{max}(h)/t_{max}(h_{re})$]. The non-monotonic magnetic field dependence of T_{max} determined experimentally displays a very similar trend when compared with most of the data obtained from MC simulations for a *noninteracting* system ($\alpha = 0$), which are also plotted in Figure 1c. We mention that the family of the MC curves of Figure 1c shows that the nonmonotonic behavior of $T_{max}(H)$ is absent for systems with a very small width of the volume particle size distribution ($\sigma = 0.100$ and 0.175) but clearly observed for higher values of σ or, more appropriately, for $\sigma \geq 0.2$.

The pairs (T_{max}, H) displayed in Figure 1c were obtained from a large number of ZFC curves of noninteracting systems, simulated by MC for σ values ranging from 0.1 to 0.75. Two selected sets of the χ_{ZFC} curves with distribution width $\sigma = 0.1$ and 0.5 are shown in Figure 2. The figure not only shows the overall trend of the $\chi_{ZFC}(T,H)$ curves but also two different behaviors found for $T_{max}(H)$: (i) the monotonic decrease of T_{max} with increasing H, for assemblies in which the volume particle size distribution of the NPs has a very narrow width $\sigma = 0.1$ (Figure 2a), and (ii) the nonmonotonic behavior of $T_{max}(H)$ for noninteracting systems of NPs with a moderate $\sigma = 0.5$ value (Figure 2b). The monotonic *decrease* of T_{max} with increasing H, as depicted in Figure 1c, for $\sigma = 0.100$ and 0.175, and Figure 2a, has been observed in previous MC simulations of *noninteracting* systems of NPs with a narrow distribution of particle volumes[5] and systems composed of monodisperse NPs.[22] In both cases,[5,22] the MC results agree well with the data of Figures 1c and 2a, given further support to the simulations performed here. Our results also indicate that the reentrant magnetic field h_{re} decreases with decreasing values of σ, following the same trend as observed experimentally (not shown), and that the nonmonotonic behavior of $T_{max}(H)$ is suppressed in systems of NPs with $\sigma < 0.2$ (see Figure 1c). Therefore, we conclude that the nonmonotonic behavior of $T_{max}(H)$ is absent in *noninteracting* samples with a narrow distribution ($\sigma < 0.2$) of uniaxial anisotropy energy or more appropriately in systems with very narrow volume particle size distribution. We have assumed arbitrarily the median value $K_0 = 1$ in the log-normal distribution for the uniaxial anisotropy energy because the reentrant behavior that appears is essentially due to the width of the distribution. Moreover, the occurrence of a maximum in the $T_{max}(H)$ dependence is experimentally observed in all samples except for the most concentrated one, with $x = 20.3$ wt % Ni, further indicating that increasing the concentration of the magnetic material alters the $T_{max}(H)$ behavior.

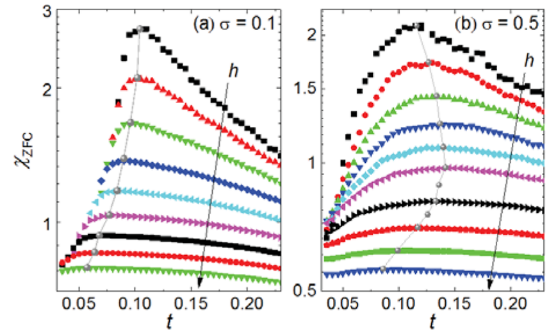

Figure 2. Curves of the magnetic susceptibility χ_{ZFC} as a function of the reduced temperature obtained from Monte Carlo simulations for a system of noninteracting NPs ($\alpha = 0$) and two different values of width of the volume particle size distribution (a) $\sigma = 0.1$ and (b) $\sigma = 0.5$. The curves were generated for increasing applied magnetic fields, indicated by the arrows. The full circle symbols mark the position of T_{max} in each curve, and the solid lines are guides to the eyes.

We turn now to the effect of dipolar interactions on the $T_{max}(H)$ behavior. The magnetic field dependent ZFC curves were obtained from MC simulations in systems with different strength of the magnetic dipolar coupling, i.e., $0.02 \leq \alpha \leq 0.5$, as displayed in Figure 3. A similar set of ZFC curves, obtained experimentally in samples with Ni NPs within the concen-

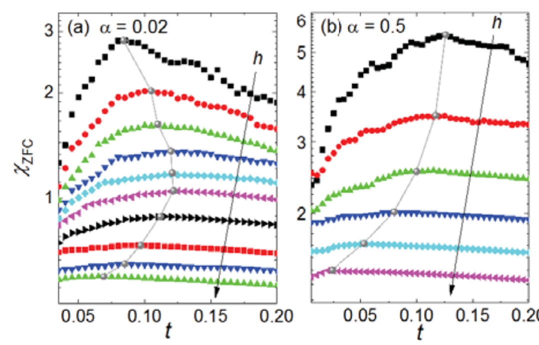

Figure 3. Magnetic susceptibility χ_{ZFC} curves as a function of the reduced temperature obtained from Monte Carlo simulations for systems with a log-normal volume particle size distribution ($\sigma = 0.5$) and different dipolar interaction strengths: (a) $\alpha = 0.02$ (weak interacting NPs) and (b) $\alpha = 0.5$ (interacting NPs). The arrows indicate the progressive increase of the applied magnetic field from the top to the bottom of the figure. Full circle symbols show the position of T_{max} for each curve, and the solid lines are guides to the eyes.

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J. Phys. Chem. C 2016, 120, 765−770

tration range 1.9–20.3 wt %, is shown in Figure 4. The results indicate the occurrence of the nonmonotonic $T_{max}(H)$ dependence in systems in which the dipolar interaction between NPs is weak, as shown in Figure 3a for $\alpha = 0.02$ and Figure 4a for $x = 4.0$ Ni wt %. Such a feature, also observed in noninteracting NPs assemblies, provided that the width of the volume particle size distribution $\sigma \geq 0.2$ (see Figure 2a), anticipates a delicate balance between the width of the volume particle size distribution of the assembly of magnetic NPs and the strength of the dipolar interaction. We also mention here that curves of Figures 3b and 4b clearly show that increasing the strength of the dipolar interaction between NPs results in a progressive suppression of a maximum in the $T_{max}(H)$ dependence. The suppression of the nonmonotonic $T_{max}(H)$ dependence occurs for values of $\alpha \geq 0.4$ and $x \geq 20.3$ wt % in the series studied, as inferred from the MC simulations and experimental results.

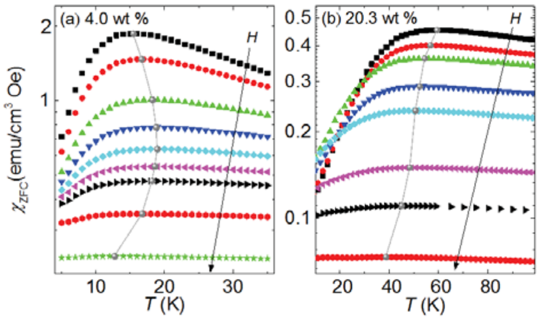

Figure 4. Temperature dependence of the magnetic susceptibility χ_{ZFC} curves of samples with (a) $x = 4.0$ and (b) 20.3 wt % Ni. Arrows indicate the progressive increase of the applied magnetic field from the top to the bottom of the figure. The full circle symbols indicate the position of T_{max} for each curve, and the solid lines are guides to the eyes.

The results displayed in Figures 3 and 4 indicate that the $T_{max}(H)$ behavior changes when the strength of dipolar interaction between particles is varied. In order to analyze this behavior, the MC data are plotted together with the data for Ni NPs in Figure 5. The figure shows the magnetic field dependence of T_{max} for the Ni NPs samples with $x = 1.9$, 2.7, 4.0, 7.9, 12.8, and 20.3 wt % in matte color and the MC results in bright color. As the dipolar interaction α *increases*, which is equivalent to *increase* the concentration x of the Ni NPs, the reentrant behavior in $T_{max}(H)$ is suppressed; i.e., the $T_{max}(H)$ behavior shows a monotonic behavior above a given magnitude of the dipolar strength. From the data displayed in Figure 5, the reentrant behavior is suppressed for values of the reduced dipolar coupling in the $0.3 < \alpha < 0.4$ interval. Comparing the results of the MC simulations with the experimental values found in the series of Ni NPs, one is lead to conclude that α values in the range 0.3–0.4 roughly correspond to Ni NPs within the interval $13 < x < 20$ wt % Ni. A careful inspection of the curves for $h/h_{re} < 1$, emphasized by the solid lines in Figure 5, also indicates that the initial increase of $T_{max}(H)$ changes noticeably with α and x. The curves shift toward higher $t_{max}(h)/t_{max}(h_{re})$ values with *increasing* dipolar interaction; i.e., the curvature of $T_{max}(H)$ changes with increasing α and x. The evolution of $t_{max}(h)/t_{max}(h_{re})$ as a function of α and x results in a monotonic decrease of $T_{max}(H)$ for $\alpha = 0.4$ in the MC simulations and $x = 20.3$ wt % in Ni NPs samples. More precisely, there is a continuous tendency of the reentrant behavior to be suppressed with *increasing* dipolar interaction between granules, further indicating that dipolar interactions affect the nonmonotonic behavior of T_{max} vs H. Therefore, the model behind the MC simulations discussed here supports the experimental observations in which the increase of the dipolar interaction results in a suppression of the reentrant behavior (see Figure 5). From the results displayed in Figures 1 and 5, one may also conclude that the occurrence of the non-monotonic behavior of $T_{max}(H)$ in systems with low fraction of magnetic NPs is related to two features: (i) the width of the log-normal volume particle size distribution function, provided that its width $\sigma \geq 0.2$, and (ii) the ratio between the dipolar coupling and the magnitude of the uniaxial anisotropy, that may not be large, i.e., $\alpha \leq 0.3$. The anomalous $T_{max}(H)$ dependence has not been observed experimentally in systems of NPs with a high volume fraction of magnetic material; instead, an expected, monotonic behavior is frequently seen, both theoretically and experimentally, in assemblies of interacting magnetic NPs.[5,6]

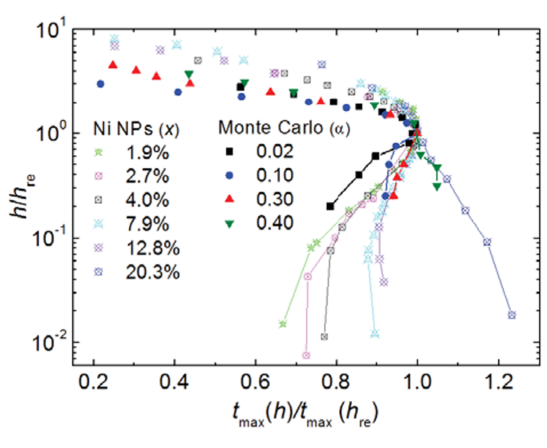

Figure 5. Representation of the ratio h/h_{re} vs $t_{max}(h)/t_{max}(h_{re})$ for samples $x = 1.9$, 2.7, 4.0, 7.9, 12.8, and 20.3 wt % of Ni, plotted in matte color, and the results of MC simulation for $\alpha = 0.02$, 0.10, 0.30, and 0.40, plotted in bright color. The solid lines are guides to the eyes.

We have shown that our MC simulations were able to capture the features displayed in the experimental ZFC curves and therefore the $T_{max}(H)$ dependence of our samples and other diluted systems of NPs. We have also inferred that the width of the volume particle size distribution σ and negligible and/or weak dipolar interactions, represented in our MC simulations by α, are the main ingredients for the observation of a maximum in the $T_{max}(H)$ behavior in diluted systems composed of magnetic NPs. However, the complex scenario involving different combinations of σ and α, along with varying temperature and H, certainly covers other magnetic properties of interest. We first mention that a nonzero value of σ, in the low temperature limit, suggests that the system is composed of two types of NPs: blocked and superparamagnetic SPM. The application of a magnetic field H causes an increase of the $M(T,H)$ of the system which is a sum of the two components, being the contribution of the SPM NPs a nonlinear function of H.[23] In the low H limit, one would expect that the contribution of the blocked NPs to $M(T,H)$ be dominant, resulting in an *increase* of $T_{max}(H)$, as we have observed experimentally in our samples and MC simulations for $\sigma \geq 0.2$. In fact, a close inspection of the data displayed in Figure 1 indicates that there is a tendency for the nonmonotonic behavior in *noninteracting* systems with very low σ values, i.e., $\sigma = 0.175$ and 0.200. Such a

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feature is reminiscent of the delicate balance between the two contributions to $M(T,H)$, further indicating that a *non-interacting* system of NPs with a volume particle size distribution width $\sigma \geq 0.2$ would exhibit the nonmonotonic behavior of $T_{max}(H)$, as predicted in the MC simulations.

Another point of interest here is the apparent increase of the mean energy barrier under applied magnetic field in the low-H limit,[7] which is certainly related to the weight between SPM and blocked NPs contributions to $M(T,H)$, both changing with H and temperature. We also mention that the nonlinear field dependence of $M(T,H)$[8,11,13,14] and the increase of the width of the energy barrier distribution,[9] interpreted as the origin of the nonmonotonic behavior of $T_{max}(H)$, are a natural consequence of a nonzero distribution width of the uniaxial anisotropy energy used in our MC simulations. In fact, the unique balance between SPM and blocked NPs contributions to $M(T,H)$ under low H is behind the observed initial increase of T_{max} with increasing H. In addition, increasing the width of the volume particle size distribution σ results in a gradual flattening of the $\chi_{ZFC}(T,H)$ curves, a behavior also observed when the applied magnetic field is increased, in excellent agreement with both experimental and theoretical $M(T,H)$ curves. Such a progressive flattening of the magnetization curves with increasing H, displayed in Figures 2 and 3, is much more pronounced in systems in which the width of the volume particle size distribution is wide, as experimentally observed in the ZFC curves of our Ni NPs (Figure 4) and those from MC simulations.

■ CONCLUSION

We have provided here a complete set of both experimental and theoretical data regarding the nonmonotonic behavior of $T_{max}(H)$ extracted from ZFC measurements in assemblies of magnetic NPs. The occurrence of such an unusual behavior, observed in samples composed of Ni NPs with $x \leq 12.8$ wt % Ni, and in Monte Carlo simulations for $\alpha \leq 0.3$, is a result of the combination of two properties of assemblies of magnetic NPs: (i) the width σ of the volume particle size distribution and (ii) the strength of dipolar interaction between NPs. We have also found, both experimentally and theoretically, that there is a progressive tendency for the suppression of the nonmonotonic behavior in two different scenarios. The first one occurs in noninteracting systems with decreasing values of σ and the second for an interacting system with increasing Ni content or, more appropriately, with increasing dipolar interaction between granules. The suppression of the nonmonotonic behavior by increasing the dipolar interaction is a natural explanation for the absence of such a feature in the $T_{max}(H)$ dependence of many experimental observations in magnetic NPs systems, provided that the concentration of magnetic material in the majority samples studied in the literature is higher than ~5 vol %.

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Notes

The authors declare no competing financial interest.

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