Slow magnetic relaxation in well crystallized, monodispersed, octahedral and spherical magnetite nanoparticles

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ABSTRACT
Thermally activated relaxation over energy barriers concurrently related to local properties and interparticle interactions constitutes a major contribution to both the coercivity and the applied field frequency dependence of that quantity. We have measured the slow magnetic relaxation of magnetite nanoparticles (NPs), synthetized by using the oxidative precipitation technique, having spherical and octahedral shapes, monodispersed size distributions and similar transverse dimensions. From our relaxation data we evaluated the temperature dependencies of a) the irreversible demagnetization susceptibility, b) the fluctuation field (associated to the thermally induced demagnetization occurring during the measuring time range) and c) the activation volume (corresponding to the demagnetization produced by the fluctuation field). We conclude that i) the irreversible susceptibility peaks in both samples at ca. 135 K (Verwey transition temperature) and ii) the monotonically increasing temperature variation of the activation volume shows the same values in both samples for temperatures below ca. 135 K and at 290 K reaches values corresponding to 10 and 30 times the average particle volume of the spherical and octahedral NPs, respectively. Those large increases of the activation volume are compatible with a transition from local to collective of the thermally activated processes.

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INTRODUCTION
The coercivity is linked to the field-induced processes through which the NPs switch magnetization.1 Those processes are triggered by the decrease in magnitude of the energy barriers protecting the remanence-like configurations from decaying towards the close-to-parallell to the demagnetizing field ones.2 For applied demagnetizing fields of the order of the coercivity those barriers have decreased in magnitude to close-to-zero values and the reversal process can also be thermally activated under constant applied field.3 The phenomenological treatment of the thermally activated relaxation is based on the Arrhenius kinetics. The model covering a distribution corresponding to a constant number of barriers per barrier energy value adequately describes the ubiquitous logarithmic time decay of the magnetization.1 From that time decay it is possible to evaluate' two main parameters: the fluctuation field, $H_f$, quantifying the field increment over the applied demagnetizing one required to account for the thermally activated demagnetization, and the characteristic volume involved in the relaxation processes: the activation volume, $v_a$.

In this work we have synthesised magnetite nanoparticles of around 20 nm in transverse dimension by oxidative precipitation of an iron (II) salt in aqueous media. We measured in these samples the temperature dependencies of their saturation magnetization, coercivity and constant applied demagnetizing field relaxation.
EXPERIMENTAL

The studied magnetite NPs were prepared as follows. An Fe(II) solution (FeSO$_4$) was quickly added to a basic solution in the presence of a mild oxidant (NO$_3$K) under stirring in an oxygen free atmosphere and the mixture was aged at 90 °C for 24 h without agitation. After that, nanocrystals were separated by magnetic decantation and washed with distilled water. The particle size is controlled by changing the nature of the base and nitrate salt and the ethanol content in the media, while the morphology is controlled by changing the final base concentration.

Particle size, shape and crystal structure were determined by transmission electron microscopy (TEM), high-resolution electron microscopy (HRTEM), and X-rays diffraction (XRD), respectively. The mean particle size and distribution were evaluated by measuring the largest internal dimension of at least 300 particles. The magnetic properties of the two samples were measured by means of a vibrating sample magnetometer, working in the temperature range from 5 K up to 290 K and by applying a maximum field of 2 T.

RESULTS

Figure 1 presents TEM and HRTEM micrographs of our magnetite nanocrystals evidencing the occurrence of the spherical (S) and octahedral (O) morphologies and good crystallinity. Particle sizes and size distributions are very similar for both morphologies (21 nm (O) and 22 nm (S), and a standard deviation of 25%). The crystal structure of the samples was identified by XRD as an inverse spinel structure without any secondary phase peak.

The temperature dependence of the saturation magnetization, $M_s$, (measured for an applied field of $1.6 \times 10^6$ A/m, see Figure 2) was non-monotonic for both morphologies (21 nm (O) and 22 nm (S), and a standard deviation of 25%). The crystal structure of the samples was identified by XRD as an inverse spinel structure without any secondary phase peak.

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The temperature dependence of the coercivity was instrumental to define the relaxation measuring fields that, for each sample and at each temperature, corresponded to five fields in the range from 95% up to 105% of the corresponding coercivities. The relaxation measurements were carried out by first taking the samples to RT and, after thermalization, slowly cooling them down to the different measuring temperatures under a dc saturating field of $1.6 \times 10^6$ A/m. Once the target temperature was stabilized and upon sample thermalization, the applied field was decreased, switched and increased in magnitude (in non-overshot control mode) until the demagnetizing, measuring field value, $H_m$, was achieved. From that instant (associated to $t = 0$) the field was kept constant and the sample magnetization was continuously recorded for a time interval of 3600 s. Upon collecting the relaxation data the sample was taken to RT and the protocol was reintitated targeting either at a different temperature or at the same temperature but at a different measuring field.

For all the fields and temperatures, the relaxation data showed an excellent agreement with a time dependence of the magnetization, $M(t) = M(t = 0) - S(H) \ln(t/t_0)$, where $S$ and $t_0$ are fitting parameters. The magnetic viscosity, $S$, depends on the measuring field and peaks at the coercivity. The parameter $t_0$ gives the measurement time scale (it took values in our fits in the range from the units to a few tens of seconds). From $S$ it is possible to evaluate the so-called magnetic viscosity coefficient, $S_V(T) = S(T)/\chi_{irr}(T)$ (where $\chi_{irr}$ is the irreversible susceptibility near the coercivity), and from $S_V$ the activation volume, $v_a(T) = k_BT/\mu_0M_s(T)S_V(T)$ and the fluctuation field associated to a measuring time of the order of the tens of seconds, $H_f(T) = 25S_V(T)$.

The evaluation of the irreversible susceptibility, $\chi_{irr} = dM_{irr}/dH$, where $M_{irr}$ is a magnetization value reached exclusively through irreversible processes under an applied field $H$, was carried out following the procedure, detailed in Ref. 7.
FIG. 2. Temperature dependencies of the saturation magnetization (left vertical axis) and the saturation coercivity (right vertical axis) of the O and S NPs.

The temperature variation of the irreversible susceptibility measured in both samples is plotted in Figure 3. Both the O and the S NPs display well-defined peaks at ca. 135 K, coincidingly with the Verwey transition which can be correlated to the good crystallinity and stoichiometry of our samples and to the disorder induced in the samples by the local proceeding of the non-diffusive monoclinic-to-cubic phase transformation (reducing the effective anisotropy and enhancing the susceptibility).

In Figure 4, we show our results for the temperature dependencies of the activation volume of our samples. The average volumes of the O and S NPs, are indicated. From the data is clear that the activation volume is only comparable to the particles volume below 30 K. This result indicates that the thermally activated magnetization reversal is only relatable to the particles morphological features at those temperatures. In agreement with this point, above 30 K and up to ca. 135 K the activation volumes of the samples are indistinguishable reaching at the latter temperature magnitudes of up 10 times the average O NPs volume. Above 135 K the activation volume of the S NPs tends to be larger than that of the O NPs reaching differences of up to 8% close to RT. This point should be ascribed to the differences between the characteristics of the monoclinic-to-inverse spinel structural transition in samples having different morphologies (and/or crystallinities).

Finally, and considering the data in Figure 5, corresponding to the temperature dependencies of the ratio between the fluctuation field values and the coercivity of the samples, it is clear that for temperatures above 225 K the fluctuation field has a magnitude larger than the measured coercivity.

FIG. 3. Temperature dependencies of the irreversible susceptibility at the coercive force demagnetizing field range.

FIG. 4. Temperature dependencies of the activation volume.

FIG. 5. Temperature dependencies of the ratio fluctuation field-to-coercivity in the O and S NPs.
CONCLUSIONS

Our results indicate that the thermally activated reversal has in our NPs a collective nature in the temperature range from 30 K up to RT (it involves characteristic volumes of up to 30 times larger than the particles average volumes). Consequently, the morphology differences between our two samples are mostly irrelevant, in the respect of relaxation, in that temperature range.

The fact that the coercivity of the O sample is higher up to RT than that of the S sample can be correlated to the differences in saturation magnetization of both samples (a larger $M_s$ was measured in the S NPs) although this point does not account for the decreasing with the increasing temperature magnitude of the coercivity differences. The degree of collectiveness (measured by the activation volume) indicates that the local demagnetizing factor, linked to the moment structures mediating the collective reversal, should evolve differently in both samples.

The fluctuation fields measured in the samples at temperatures slightly below RT are larger than the corresponding coercivities, implying the occurrence at these temperatures of first quadrant irreversible reversal and therefore reduced hysteresis losses. This result indicates that the thermal activation is a major aspect on determining the hysteretic parameters of our NPs and that their optimization should be taken explicitly into account.

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