# Magnetic relaxation measurements of $\alpha$-$Fe_2O_3$ antiferromagnetic particles below 1 K

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In this paper we report magnetic relaxation data for antiferromagnetic $\alpha$-$Fe_2O_3$ particles of 5-nm mean diameter in the temperature range 0.1–25 K. The average spin value of these particles $S \simeq 124$ and the uniaxial anisotropy constant $D \simeq 1.6 \times 10^{-2}$ K have been estimated from the experimental values of the blocking temperature and anisotropy field. The observed plateau in the magnetic viscosity from 3 K down to 100 mK agrees with the occurrence of spin tunneling from the ground state $S_Z = S$. However, the scaling $M$ vs $T \ln(\nu_0 t)$ is broken below 5 K, suggesting the occurrence of tunneling from excited states below this temperature.

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The search for candidates to study the quantum oscillations of spin between opposite orientations is of major interest today for both basic and applied purposes. There are two areas in which this is extremely important: the study of the spin quantum coherence in mesoscopic systems,[1–3] and the assessment of magnetic units as hardware for quantum computation.[4–6]

The rate of magnetic relaxation of a single domain particle associated to thermal fluctuations is $\Gamma = \nu \exp(-U/T)$ where $U$ is the energy barrier and $\nu$ is the attempt frequency. In the case of ensembles of small particles with a distribution of volumes, the magnetization depends on time, in the case of thermal relaxation, only through the combination $T \ln(\nu t)$. The occurrence of magnetic relaxation in a fine particle system at temperatures where thermal fluctuations vanish has been explained in terms of quantum tunneling.[7,8] Many of the experiments carried out in magnetic systems have been performed at temperatures above 1 K and using ferro- and ferrimagnetic particulate systems with interaction between particles.[7,8] There are also interesting measurements of ferrimagnetic and ferromagnetic single particles.[9,10] In this paper we show data of relaxation experiments down to mK for a system of independent antiferromagnetic particles with a narrow size distribution.

$\alpha$-$Fe_2O_3$ is an antiferromagnet ($T_N = 960$ K) which undergoes a spin-flip transition at the Morin temperature, $T_M = 263$ K. Below $T_M$ it is a uniaxial antiferromagnet with the spins aligned along the trigonal (111) axis, whereas above $T_M$ is a canted antiferromagnet with the spins perpendicular to (111), except for a slight canting (0.13°) from the basal plane, which results in a small net magnetic moment. There is, however, another contribution to the net spin of these particles. This is associated with the number of noncompensated spins expected from the randomness of the surface core. The Morin temperature reduces as the particle size decreases tending to vanish for particles smaller than about 8 nm.[11] The antiferromagnetic $\alpha$-$Fe_2O_3$ particles were prepared from precursor FeOOH particles following the route proposed by Zysler *et al.*[12] The x-ray powder-diffraction pattern shows the hematite structure corundum type of the particles. Morphological characterization of the particles was made by using both a commercial light dispersion equipment before drying the solution and a 200-keV transmission electron microscopy. The particles show a platelet shape.[12–14] The size distribution is centered at 5 nm and comprised between 3 and 7 nm. Electron spin-resonance (ESR) measurements were made at the $X$ band (9.4 GHz) at temperatures down to 2 K. No single-ion resonance line appears in the spectrum; that is, our sample is free of paramagnetic impurities.

Magnetization measurements down to 1.8 K were performed by using a Quantum Design superconducting quantum interference device (SQUID) magnetometer. The very low-temperature magnetic measurements were carried out by using a top loading $^3$He-$^4$He dilution refrigerator (Oxford Kelvinox) which has incorporated a 5-T superconductor magnet. The sample is inside the liquid mixture and its temperature may be varied between 50 mK and 1.2 K. The magnetic moment of the sample is registered using a superconductor gradiometer by the extraction method. This gradiometer is coupled through a superconducting transformer to a Quantum Design dc SQUID which is placed near the 1-K pot. The temperature of the dc SQUID is kept constant as it is thermally linked to the 1 K pot. The dc SQUID has also been shielded from the magnetic field created by the superconductor magnet and the magnetometer has been calibrated by using pure paramagnetic samples.

In Fig. 1 we show the low-field ($H = 300$ Oe) magnetization measurements down to 1.8 K. The zero-field-cooled (ZFC) magnetization is mainly due to the fraction of particles that behave superparamagnetically at a given $T$, while the field-cooled (FC) magnetization corresponds to the equilibrium value. The inset of Fig. 1 shows the ZFC data obtained with the dilution refrigerator down to the lowest temperature ($T = 100$ mK). The data for both ZFC and FC above 4 K are in agreement with those reported by Bødker

 

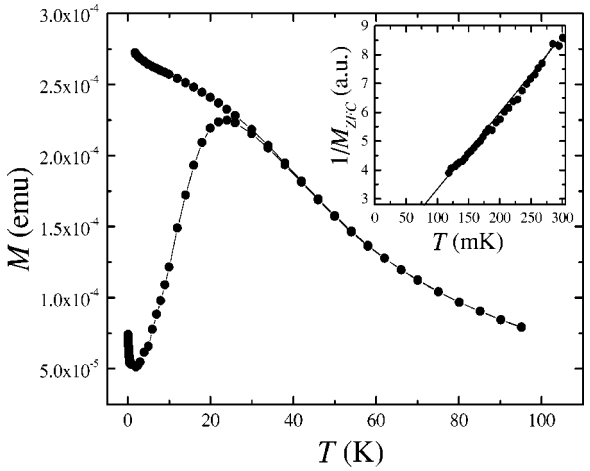


FIG. 1. ZFC and FC magnetization curves. The inset shows the linear dependendence of $1/M_{ZFC}$ on temperature in the millikelvin regime. The extrapolation of these data to zero temperature gives $\theta_c \simeq 0$ mK.

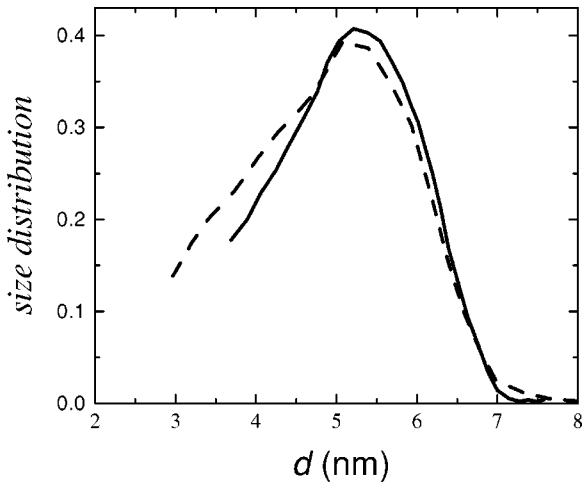


FIG. 2. Size distribution of $\alpha$-$Fe_2O_3$ particles deduced from the ZFC and FC curves using Eq. (2) (dashed line) and from the $M$ vs $T\ln(\nu_0 t)$ plot (continuous line).

*et al.*[15] from magnetic and Mössbauer measurements performed in the Kelvin regime on particles of 16-nm average size. The blocking temperature for our particles is, however, larger than that estimated for the particles of Bødker *et al.*[15] which may be due to the increase of the surface anisotropy when reducing the size of the particles.

The zero-field-cooled magnetization at a given temperature, field, and time is given by[7]

$$M(T,H,t) = \frac{m_0^2 H}{2T}\int_0^{V_B(T,t)} dV f(V) V^2, \qquad (1)$$

where $m_0$ is the magnetic moment per unit volume of the material of the particle, $f(V)$ is the volume distribution of the particles, $V_B(T,t) = (k_B T/K)\ln(\nu_0 t)$ is the blocking volume at a given temperature $T$ and time $t$, $\nu_0$ is the attempt frequency, and $K$ is the magnetic anisotropy energy density. At $T > T_B$, the average blocking temperature, the integral of Eq. (1) becomes constant because the moments of most of the particles are unblocked. That is, above the blocking temperature the ZFC magnetization should follow the $1/T$ superparamagnetic Curie law, as it is experimentally observed. In other words, the origin of the $1/T$ increase in the ZFC magnetization (time window of 1 s) is in slower process than expected from paramagnetic impurities, since they are not detected by EPR measurements (time window of $10^{-10}$ s). Hence this $1/T$ variation may correspond to quantum processes affecting the particles.

At $T \ll T_B$, the ZFC magnetization depends on the volume distribution function because the fraction of superparamagnetic particles contributing to the magnetic signal decreases when the temperature decreases. Below 1 K, however, the ZFC magnetization increases when temperature decreases, with a $1/T$ dependence down to the lowest temperature of 100 mK. This behavior cannot be due to paramagnetic impurities, since their presence should be detected by EPR measurements, which is not the case. This result can be explained by Eq. (1) if the relaxation volume $V_B$ does not depend on temperature below 1 K. That is, in the presence of quantum relaxation, the temperature in the definition of $V_B$ is replaced by the temperature $T_c$ of the crossover from the classical to the quantum regime. At $T < T_c$, quantum transitions, independently of the volume distribution, result in the ZFC curve proportional to $1/T$. It may be concluded therefore that there is a fraction of particles whose magnetic moments never get blocked due to quantum tunneling effects and behave quantum superparamagnetically.

The FC data split from the ZFC data at $T = T_{max}$ as they correspond to the equilibrium magnetization at each temperature. For temperatures lower than 5 K the FC data grow with temperature following a Curie law until the lowest temperature of 100 mK. The Curie-Weiss temperature $\theta_C$ deduced from the extrapolation to zero temperature of the FC data measured below 1 K (see inset in Fig. 1) is $\theta_C \simeq 2$ mK, suggesting a very weak interaction between the magnetic particles.[8] Using the temperature variation of the so-called isothermal remanent magnetization, $M_{TRM} = 2M_{ZFC} - M_{FC}$,[16–18] we have deduced the volume distribution of particles (see dashed lines in Fig. 2).

All isothermal magnetization curves, for $T > T_B$, are well fitted by Boltzmann's statistics and follow a $H/T$ scaling when considering the random distribution of easy axis and the temperature variation of the magnetic moment of the particles. Below $T_B$, the $M(H)$ curves show hysteresis. Below 1 K the cycles close at $H \simeq 3$ T, which roughly represents the highest particle anisotropy field $H_{an}$. The continuous increase of both coercitivity and anisotropy field when reducing the temperature below the blocking suggests that the Morin transition does not take place in these small particles.[11]

Magnetic relaxation measurements were performed down to 100 mK. In order to make easier the comparison of the data obtained above (Quantum Design SQUID magnetometer) and below (dilution refrigerator) to 1.6 K, we have followed the same procedure in all the temperature range, from 100 m K to 30 K. At each temperature, a high magnetic field, $H = 4$ T, is applied and after 1 h it was switched off. The

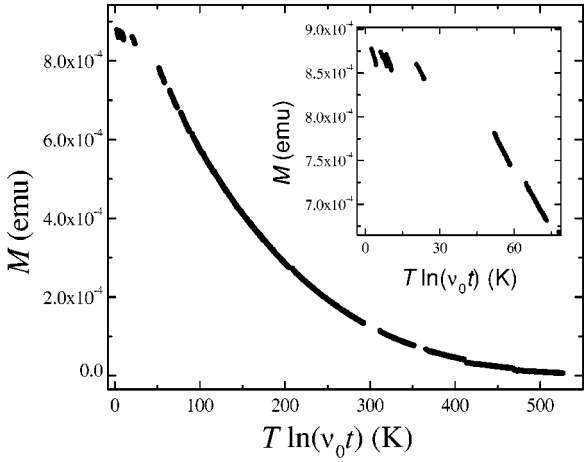


FIG. 3. Magnetization of $\alpha$-$Fe_2O_3$ particles versus $T\ln(\nu_0 t)$. The best fit has been achieved using $\nu_0 = 10^8$ sec$^{-1}$.

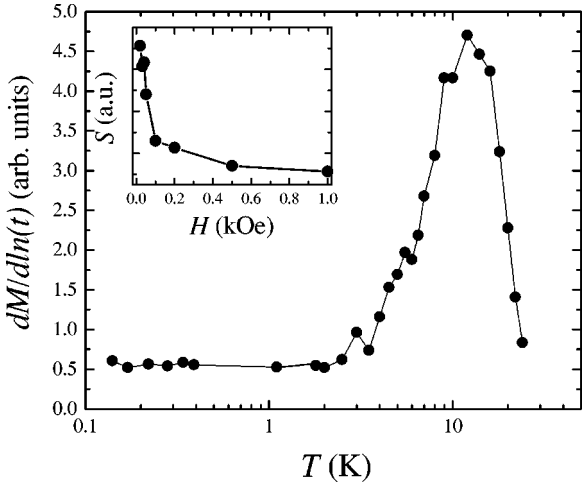


FIG. 4. The temperature dependence of the magnetic viscosity $S$ for the $\alpha$-$Fe_2O_3$ particles. The inset shows the variation of $S$ with field at $T = 3$ K.

variation of the total magnetization with time was recorded for a few hours. The $\ln(t)$ relaxation was observed for all temperatures below the blocking temperature. Figure 3 shows the relaxation data plotted as $M(t)$ vs $T\ln(\nu_0 t)$. The relaxation data collected above 5 K assemble nicely into the universal curve expected in the case of purely thermal relaxation.[7,16] The best fit of this scaling is obtained using $\nu_0 = 10^8$ Hz. Below 5 K (see inset of Fig. 3), there is a systematic departure from the universal curve, suggesting that nonthermal relaxation phenomena are occurring at these low temperatures until the lowest temperature $T = 100$ mK. The derivative, $dM/d[T\ln(t/\tau)]$, of the master curve in the thermal regime represents the volume/barrier height distribution (see solid lines in Fig. 2). It can be then concluded from both the relaxation measurements and the low-field magnetization data, that the peak at 5 nm in the distribution of particle sizes is in good agreement with the data from electron microscopy and light scattering.

The magnetic viscosity $S$, which is independent from the initial and final states, is

$$S = \frac{1}{M_0 - M_{eq}} \frac{dM}{d\ln t} \propto \frac{TV_B f(V_B)}{K} \propto T^2, \tag{2}$$

and its values have been deduced (see Fig. 4) from the $M(t)$ data. As Eq. (3) reads, the viscosity should go to zero as temperature decreases if only thermal relaxation is considered. On the other hand, the viscosity values between 3 K and 100 mK remain constant suggesting the occurrence of quantum relaxation phenomena. It has also been deduced from magnetic relaxations at different fields that the magnetic viscosity monotonically decreases as a function of the magnetic field (see the inset of Fig. 4), reflecting the existence of a maximum relaxation at zero field. This could be due to resonant spin tunneling between matching spin levels.[19]

Note that the distribution function $f(V) \sim V^{-2}$, would mimic the plateau in the viscosity, but it would result also in a constant ZFC magnetization and the preservation of the $M$ vs $T\ln(\nu_0 t)$ scaling in all the temperature range, in disagreement with the experimental findings. The existence of canted spins in a surface layer in a spin-glass-like phase has also been proposed to explain the low-temperature magnetic properties of some ferri- and antiferromagnetic particles.[20–22] Surface spins have multiple configurations for any orientation of the core magnetization, and the distribution of energy barriers should be $f(E) \sim 1/E$. This could explain the constancy of the viscosity at temperature $T < 3$ K, but it cannot explain the rest of our low-temperature experimental findings.

Let us discuss our results in the frame of the discrete spin level structure existing in the two potential wells of the magnetic anisotropy. The spin Hamiltonian of these nanosized antiferromagnetic particles with a platelet shape may be written, as a first approximation, in terms of the dominant uniaxial anisotropy term $DS_z^2$ and the Zeeman term due to the interaction of the net spin $S$ of the particles with the external magnetic field

$$H = -DS_z^2 + H' - g\mu_B SH. \tag{3}$$

Due to the size distribution and the nonuniform shape of particles we expect to have a distribution of values for $D$ and $S$. $H'$ stands for other anisotropy terms. The symmetry-violating terms in the spin Hamiltonian of Eq. (3) inducing tunneling are those associated with the transverse component of both the magnetic field and magnetic anisotropy. The values of $D$ and $S$ in Eq. (3) represent the mean values for all particles. Taking into account that: (i) The average barrier height, $U \equiv DS^2$, is proportional to the average blocking temperature, $T_B \simeq 12$ K, $U = T_B \ln(\nu_0 t) = 248$ K, where $\nu_0 = 10^8$ Hz and $t \simeq 10$ sec is the experimental time window, and (ii) the anisotropy field, $H_{an} = 2DS \simeq 3$ T, is the field value that eliminates the barrier height between the two spin orientations, we have estimated $S = 124$ and $D \simeq 1.6 \times 10^{-2}$ K. Writing the relevant barrier height as $U = KV$, we find that $K \simeq 8 \times 10^5$ erg/cm$^3$.

The temperature $T_c$ of the crossover from quantum to thermal superparamagnetism[7] may be roughly estimated from $T_c \simeq \mu_B (H_\parallel H_{ex})^{1/2}$, where $H_\parallel \simeq 3$ T and $H_{ex}$ is the ex-

change field which may be estimated from the Néel temperature, $T_N = 960$ K. We obtained $T_c \simeq 5$ K.

The first term of Eq. (3) distributes the spin levels in the two wells of the magnetic anisotropy separated by the energy barrier $U$. The spin level, $m = S_Z$, contributing to the magnetic signal at each temperature $T$, and for fields much smaller than $H_{an}$, satisfies $D(S^2 - m^2) \simeq 20T$, that is at $T \simeq T_B$ the contributing levels are those near the top of the barrier, $m = 0$, while at $T \ll T_B$ only the ground state $m = S$ contributes to the magnetization relaxation. This explains why at temperatures just below the blocking the relaxation is purely thermal. At lower temperatures, however, the thermal relaxation above the barriers competes with quantum tunneling from the excited states. The fact that the scaling $M$ vs $T \ln(\nu_0 t)$ is broken below 5 K should correspond therefore to the occurrence of tunneling effects from the above-mentioned levels. The plateau in the viscosity below 3 K should reflect the quantum tunneling process from the ground state $S_Z = S$, in agreement with the fact that at these low-temperatures only the level $S_Z = S$ is populated. Moreover, the very low temperature ZFC and FC magnetization curves obey the $1/T$ Curie law suggesting that the inverse of the tunneling frequency matches the experimental window time and the particles are ''seen'' superparamagnetically on our resolution time.

In conclusion, we have presented magnetic relaxation data on antiferromagnetic $\alpha$-$Fe_2O_3$ down to 100 mK, for which the most plausible interpretation is the occurrence of spin tunneling.[1,18,19,23,24] The decrease of the viscosity when magnetic field increases agrees well with the discrete level structure in the two wells.


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