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Abstract. We have studied the response of a system of small (~4 nm) ferrimagnetic particles to a field reversal at low temperature (0.6 to 12 K). The reversal of the particle magnetic moments through the anisotropy barriers is shown to be governed by thermally activated dynamics down to 0.6 K, with no evidence for quantum effects. We propose a data analysis in terms of the unique variable $T \cdot \ln(\frac{T_0}{T})$, which accounts for a non-constant distribution of anisotropy barriers.

1. Introduction.

Since the pioneering works of Louis Néel on magnetic grains [1, 2], superparamagnetism has been widely studied [3]. The interest in this field has been recently revived by theoretical studies [4, 5] of the magnetization reversal of small particles through their anisotropy barrier, which have shown that quantum tunneling processes [6, 7] could have a significant contribution for small but macroscopic particles (a few nm) at not very low temperatures (of order 1 K).

The challenge of evidencing a new example (actually the second one, after superconductivity and related junction phenomena) of the irruption of quantum mechanics in our macroscopic world has motivated a lot of experimental work [8-11]. In most of these studies, the samples are collections of magnetic objects of different sizes and shapes, supposedly magnetically decoupled. They present a wide distribution of anisotropy energy barriers (except perhaps in [11]), at least wide enough to produce (through the drastic exponential dependence of characteristic times on barrier heights) a quasi-logarithmic time-dependence of the relaxation. The logarithmic slope of the relaxation curve is defined as the magnetic viscosity; its temperature dependence reflects the thermal (or possibly quantum) nature of the excitations, but is also weighted by the energy barrier distribution. In the present literature, numerous situations [8-10] in which the magnetic viscosity fails to decrease regularly for decreasing temperature are ascribed to quantum tunneling processes. In this paper, we present an experimental study of small (ca. 4 nm) ferrimagnetic $\gamma$-Fe$_2$O$_3$ particles. Down to 0.6 K, the results remain compatible with
thermally activated dynamics; we show how this can be checked without a priori assumptions concerning the distribution of anisotropy barriers.

2. Sample.

Maghemite $\gamma$-$\text{Fe}_2\text{O}_3$ is a metastable phase of hematite $\alpha$-$\text{Fe}_2\text{O}_3$. It has the inverted spinel structure of the magnetite $\text{Fe}_3\text{O}_4$, with vacancies on the B-site and a ferrimagnetic arrangement between the A and B sites [12]. X-ray diffraction measurements [13] have shown that the vacancies do not order at long range in particles less than ca. 20 nm in size. The Curie temperature is 590 °C.

Small particles of $\gamma$-$\text{Fe}_2\text{O}_3$ can yield electrostatically-stabilized dispersions in aqueous medium [14]. The acidity of the medium controls the density of electrical charges on the surface of the particles. The surface electrical charge promotes particle-solvent interactions and particle-particle repulsions which compete with Van der Waals and magnetostatic interactions. Via the pH, it is thus possible to control the particle aggregation [15-17]. Aggregation is minimal near pH = 2 and maximal near pH = 7 where flocculation occurs because of surface charge canceling.

Colloids of $\gamma$-$\text{Fe}_2\text{O}_3$ were prepared according to [18]. The precipitate obtained by alkalizing an Fe$^{2+}$-Fe$^{3+}$ aqueous mixture with NaOH was treated with HClO$_4$ until the ratio Fe$^{2+}$/Fe$^{3+}$ in the particles was $\sim$ 0.03. On dispersal in water, it yielded a sol of pH = 2.1. The dispersion was frozen by adding a stiffening polymer (polyvinyl alcohol). Electron microscopy observations of the composite have shown that the particles are spheroidal, their diameter being distributed around a peak value of 4.2 nm, with a full width at half maximum (FWHM) of 3.0 nm. The amount of Fe in the composite was measured to be $0.37 \times 10^{-3}$ Fe mole/g, and the composite density is equal to 1.33 g/cm$^3$. This yields a separation of the particles, from center to center, of the order of 6 times their mean diameter, assuming that the particles are homogeneously distributed in the sample and have a density of 4.87 g/cm$^3$.

3. Static properties.

The magnetic measurements have been performed in a pumped He-3 cryostat. The magnetization was measured by extracting the sample out of the detection coil while integrating the induced voltage. The sensitivity of the set-up corresponds to a magnetic moment of a few $10^{-5}$ emu. All along this paper, the magnetization values in emu have been normalized to the volume of $\gamma$-$\text{Fe}_2\text{O}_3$ (which amounts to $\sim$ 0.5% of the total volume of resin).

Figure 1 shows the magnetization curve obtained at 4.3 K during a field cycle from $H = 0$ to 15 kOe and back. The sample has been cooled in zero field from 40 K, but still shows an initial zero-field magnetization of 32 emu related to previous field history.

Upon increasing the field, no real saturation is found; around 5 kOe, the magnetization becomes reversible but continues to increase roughly linearly with a weak slope $dM/dH \simeq 3.2 \times 10^{-3}$ emu. This continuous increase, also observed in [17], is likely to be due to a progressive increase of the net ferrimagnetic moments for increasing field; the observed slope is indeed of the same order as the value which can be crudely estimated from the ratio of the applied to exchange fields [19]. Linearly extrapolating the high-field behavior to zero field, we can determine a “saturated magnetization at zero field” $M_{so} = 191$ emu (see Fig. 1).

After magnetizing the sample under a field of 15 kOe, the remanent magnetization found at zero field is 92 emu = 0.48 $M_{so}$. This proportion is very close to the 50% value which is to
be expected when all magnetic moments are oriented, along their randomly distributed easy axes, in the direction selected by the previously applied field [19]. The coercive field which suppresses this remanence is \( H_c = 500 \text{ Oe} \).

The anisotropy energy \( K_A \) of the particles can be calculated from the magnetization curve in figure 1. It corresponds to the work needed to magnetize the sample up to saturation. We estimate \( K_A \) by summing the work up to \( M_{so} \).

\[
K_A = \int_0^{M_{so}} H \cdot dM \simeq 8 \times 10^6 \text{ erg/cm}^3.
\]  

(1)

This value is an average over the anisotropy directions of the particles with respect to the field. In addition to the bulk magnetocrystalline effects, it is expected to include other important contributions: the shape (departure from sphericity) of the particles plays of course an important role, together with possible surface effects and constraints due to magnetostriction [3].

Figure 2 presents the variation of the sample magnetization with temperature under a 300 Oe field. The sample has initially been cooled in zero applied field from 80 K to 4.3 K. A residual magnetization \( M_0 = 94 \) emu is found at 4.3 K. This remanence, which appeared after previous measurements under higher fields, could not be suppressed; it arises from much larger magnetic entities than those which can respond at low temperatures and low fields. However, all the forthcoming measurements (including the relaxations, Sect. 5) have been done under these same conditions. In order to only show the response of the sample to a 300 Oe field applied at 4.3 K, we have subtracted \( M_0 \) from the results in figure 2. The zero-field cooled (ZFC) curve shows a broad peak around 13 K; this temperature corresponds to the blocking of objects of a typical volume \( V_b \) such that

\[
\frac{K_A \cdot V_b}{k_B \cdot T} = \ln \frac{t}{\tau_0}
\]  

(2)

Choosing \( K_A = 8 \times 10^6 \text{ erg/cm}^3 \) (our result), \( t = 1000 \) s (ZFC experimental time scale) and \( \tau_0 = 10^{-10} \) s (see below in Sect. 4), \( T \cdot \ln(t/\tau_0) \simeq 30 \) and we obtain a volume \( V_b = 6.7 \times 10^{-20} \text{ cm}^3 \), equivalent to spheres of diameter 5.0 nm.
Fig. 2. — Zero-field cooled (ZFC) and field-cooled (FC) magnetization as a function of temperature, for a field of 300 Oe. The frozen magnetization $M_0 = 94$ emu found at 4.3 K after zero-field cooling and before applying the field has been subtracted from the data in order to emphasize the effect of the field.

The broadness of the peak in figure 2 indicates that the distribution of energy barriers is very wide. Actually, the peak of the ZFC curve does not correspond to the peak of the size distribution. For increasing temperature, larger and larger objects align with the field; beyond the peak of the size distribution, the objects of larger sizes become less numerous, but they contribute significantly to the enhancement of the magnetic response because of their larger magnetization. It can be checked easily that the ZFC magnetization peaks around temperatures corresponding to one or two standard deviations above the mean value of a Gaussian distribution.

On the other hand, our size determination may be underestimated for the following reasons: (i) neglecting the temperature variation of the remanence $M_0$ may lower the position of the ZFC peak, (ii) the 300 Oe field somewhat reduces the anisotropy barriers, and (iii) zero-field cooling from only 80 K leaves out the contribution of the largest objects with a higher blocking temperature. We therefore consider that our size estimate remains approximate; nevertheless, it agrees fairly well with the mean value of 5.2 nm deduced from Mössbauer measurements [20, 21] and with the peak value of 4.2 nm (3 nm FWHM) observed by electron microscopy.

4. Relaxation dynamics: general remarks.

We have probed the slowing down of the dynamics of the particles with decreasing temperature by measuring the magnetization relaxation in response to a field reversal at low temperature. In the fictitious case of a sample constituted of strictly identical particles, all oriented in the same direction, the magnetization reversal implies crossing barriers of a unique value $U$; this gives rise to an exponential decay:

$$M(t) = M^{FC}(-H) + \Delta M^{FC} \exp\left(-\frac{t}{\tau(U)}\right),$$  \hspace{1cm} (3)

where $\Delta M^{FC} = M^{FC}(+H) - M^{FC}(-H)$ is the total magnetization excursion between the field-cooled values corresponding to the opposite values of the field, and

$$\tau(U) = \tau_0 \cdot \exp\left(\frac{U}{k_B T}\right)$$  \hspace{1cm} (4)
is the characteristic time for crossing, by thermally activated dynamics, a barrier $U$ at temperature $T$ with an attempt time $\tau_0$.

In the realistic case of a distribution $P(U)$ of anisotropy barriers $U$, equation (3) is modified to

$$M(t) = M^{\text{FC}}(-H) + \Delta M^{\text{FC}} \cdot \int_0^\infty \exp\left(-\frac{t}{\tau(U)}\right) P(U) dU$$

(5)

where the summation runs over the whole barrier distribution. Due to the exponential dependence of $\tau$ on $U$, the function $\exp\left(-\frac{t}{\tau(U)}\right)$ in the integrand increases very abruptly from 0 to 1 around the value of $U$ such that $\tau(U) = t$. Namely, for e.g. $t = 100$ s, the function is equal to 0 for $U < 26k_B T$ and equal to 1 for $U > 33k_B T$ within a 0.5% accuracy. Equation (5) is thus very well approximated by

$$M(t) \simeq M^{\text{FC}}(-H) + \Delta M^{\text{FC}} \int_{U_t}^\infty P(U) dU$$

(6)

where $U_t = U(\tau = t) = k_B T \cdot \ln(\frac{1}{\tau_0})$. Equation (6) shows that the main dependence of the magnetization relaxation on time and temperature occurs through the variable $U_t = k_B T \cdot \ln(\frac{1}{\tau_0})$; in other words, most of the magnetization change at temperature $T$ and time $t$ is due to crossing of barriers of order $U_t = k_B T \cdot \ln(\frac{1}{\tau_0})$. This famous property has already been widely used to explain some aspects of the dynamics of spin glasses [22, 23] and of randomly disordered ferromagnets [24, 25].

In order to describe magnetic viscosity measurements, let us now consider the logarithmic derivative of the magnetization:

$$\frac{dM(t)}{d\ln t} = \Delta M^{\text{FC}} \int_0^\infty \frac{t}{\tau(U)} \exp\left(-\frac{t}{\tau(U)}\right) P(U) dU$$

(7)

$$= \Delta M^{\text{FC}} \int_{\ln \tau_0}^\infty \frac{t}{\tau} \exp\left(-\frac{t}{\tau}\right) P(k_B T \cdot \ln(\tau/\tau_0)) k_B T \, d\ln \tau.$$  

(8)

Within exactly the same approximation as above (from Eq. (5) to Eq. (6)), the function $\frac{t}{\tau(U)} \exp\left(-\frac{t}{\tau(U)}\right)$ is equal to zero everywhere except around $t = \tau$, i.e. $\frac{U}{k_B T_\tau} = 30 \pm 3$. The magnetic viscosity therefore reads:

$$\frac{dM(t)}{d\ln t} = \Delta M^{\text{FC}}(T) \cdot P(k_B T \cdot \ln(\frac{t}{\tau_0})) \cdot k_B T.$$  

(9)

In the case of spin glasses [26], it has been taken advantage of this property to estimate the spectrum of response times from the measured magnetization relaxation.

In an experiment performed at a fixed temperature $T$, the range of barriers which can be probed during experimental times $t$ (such as, typically, $10^3 < t < 10^4$) is limited to

$$\frac{U}{k_B T} \sim \ln \frac{t}{\tau_0} \sim 25 - 35.$$  

(10)

If $P(U)$ can be considered constant within this range, equation (10) shows that a linear $\ln t$ dependence of the relaxation will be obtained at each temperature. This is the case if the number of particles with volume spanning a ±15% range does not vary too abruptly (assuming
that the anisotropy barrier is proportional to the volume). However, concerning the temperature dependence of the measured viscosity, it may become more difficult to consider that $P \left( k_B T \cdot \text{Ln}\left( \frac{t}{T_0} \right) \right)$ does not vary significantly over $T$-variations of a factor 10 to 20. Any departure from a strict proportionality to temperature of the viscosity [9, 10] can as well be ascribed to a $P \left( k_B T \cdot \text{Ln}\left( \frac{t}{T_0} \right) \right)$ variation as to possible non-thermal dynamics, as was also emphasized in [8, 24]. We argue that a scaling of the results as a function of the unique variable $T \cdot \text{Ln}\left( \frac{t}{T_0} \right)$ substantially helps to remove this difficulty.

5. Relaxation dynamics: measurements.

The relaxation measurements have been performed along the following procedure. The sample is first heated to 50 K, and a +300 Oe field is applied; then the sample is field-cooled down to the measurement temperature $T_0$ (between 0.6 and 12 K). We have checked that the field-cooled magnetization at $T_0$ does not show any relaxation in our range of time, nor any cooling rate dependence. Then, the field is reversed from +300 to −300 Oe, and the magnetization relaxation at $T_0$ towards the new equilibrium state under −300 Oe is recorded from a few seconds to a few hours.

Figure 3 displays a few typical relaxation curves. At temperatures below 5 K, we have measured the magnetization by extracting the sample on a twice shorter range than at higher temperatures, in order to minimize the weak heating related to the movement. This results in slightly more scattered data, as can be seen from figure 3 where both procedures are compared at 4.3 K. As a first approximation, each of the curves can indeed be considered linear in $\text{Ln} \ t$, although a careful examination reveals a slight upwards (resp. downwards) curvature for higher (resp. lower) temperatures, which will be interpreted below.

\[ \text{Fig. 3. — Typical relaxation curves at } T_0 = 11.1, 4.3 \text{ and } 1.10 \text{ K, obtained after field-cooling the sample from } 50 \text{ K to } T_0 \text{ under } +300 \text{ Oe, and reversing the field to } -300 \text{ Oe at } T_0. \text{ The curves have been arbitrarily shifted along the vertical scale. At low temperatures, the magnetization has been measured with a shorter extraction range, yielding more noisy data; both procedures are compared at } 4.3 \text{ K.} \]

For each of the curves, we have determined an average slope $dM/d\text{Ln} \ t$ by fitting a linear $\text{Ln} \ t$ behavior in the 5 to 6000 s range. We have divided (according to Eq. (9)) the slope by $\Delta M^{FC}(T)$; the latter quantity shows a 7% variation in the 0.6 to 12 K range explored. This
"corrected viscosity" is displayed in figure 4 as a function of temperature. Between 0.6 and 7 K, a nice proportionality to temperature is observed, which – within the experimental accuracy – can extrapolate to a zero value at zero temperature. As far as \( \mathcal{P}(U = T \cdot \ln(\frac{t}{T_0}) \) can be considered constant, the \( T \)-proportionality is characteristic of purely thermally activated processes; but since the explored temperatures vary from 0.6 to 12 K, the concerned energy barriers vary by the same factor 20, and there is no guarantee that the distribution \( \mathcal{P}(U) \) of the particles remains constant over such a range. A limit to this approximation can be seen in the viscosity data above 8 K, which show a saturation: the most likely explanation is that such larger particles are significantly less numerous than the smaller ones. This, in turn, prevents us from a simplistic interpretation of the low-temperature data: a departure from pure thermal activation, due e.g. to the influence of quantum tunneling processes, could be hidden by a decrease of the particle distribution for smaller sizes.

![Graph](image)

**Fig. 4.** — Viscosity data as a function of temperature. The mean logarithmic slope \( \frac{dM}{d\ln t} \) \((t \text{ in s})\) of the relaxation curves has been normalized to the total magnetization excursion \( \Delta M_{\text{FC}}(T) \) between the two field-cooled values measured with +300 and -300 Oe.

A natural presentation of the data [22, 23] follows from equation (6): one can try to plot all relaxation curves at all temperatures as a function of the single variable \( T \cdot \ln(\frac{t}{T_0}) \), which is the magnitude of the energy barrier which strongly dominates the dynamics at time \( t \) and temperature \( T \). As far as the dynamics is thermally activated, all data can be expected to fall onto a single continuous curve. The more drastic approximation of a constant distribution of barriers would imply that this curve be a straight line; this approximation is not needed any more, since the distribution \( \mathcal{P}(U) \) is now simply proportional to the slope of the curve.

The check of continuity in the \( T \cdot \ln(\frac{t}{T_0}) \) plot necessitates a reliable knowledge of the total magnetization (a measurement of the only drift with time of the magnetization would not be sufficient). We have indeed measured this total value for all data points; but, as noticed above, the sample includes a frozen magnetization which slightly depends on the history. When plotting our raw relaxation data as a function of \( T \cdot \ln(\frac{t}{T_0}) \), we have observed that, following the chronological order of data taking, our results were assembling onto three parallel curves, shifted from each other by a few emu, and corresponding to three series of measurements between which the sample had been kept several days at room temperature. We have therefore attributed these two small shifts to a variation at room temperature of the remanent magnetization (amounting to 7 and 5% of the remanence), and corrected for them. The result is presented...
in figure 5: all relaxation curves at all temperatures assemble in a unique curve. The best continuity of this curve is obtained by choosing $\tau_0 = 10^{-10}$ s; this is a rather sensitive test for $\tau_0$, since the continuity is already somewhat downgraded (over the whole temperature range) for choices of $10^{-9}$ or $10^{-11}$ s. This value, a little bit higher than the typical attempt times of paramagnetism, is indeed of the correct order of magnitude when compared with the classical models of superparamagnetism [3]. The inset of figure 5 shows a zoom of the low-temperature region. Indeed, a very slight tendency to a departure from thermal activation at the lowest temperatures 0.6-0.8 K may be suspected, which appeared also in the viscosity plot of figure 4; complementary data should be of interest, but were beyond the possibilities of the present experiment.

![Fig. 5](image)

**Fig. 5.** — All relaxation curves at all temperatures are plotted here as a function of $T \cdot \ln(t/\tau_0)$ [22, 23] (in Kelvin), which is the typical energy barrier crossed by thermal activation at temperature $T$ after a time $t$. The inset is a zoom of the low-temperature region.

The master curve in figure 5 shows a slight curvature, varying from negative to positive for increasing values of the main barrier height $T \cdot \ln(\frac{t}{\tau_0})$. This is in agreement with a weak but systematic trend already observed on the relaxation curves at different temperatures (see Fig. 3). From this we can confirm that the distribution of barriers is not flat, but has a maximum (inflection point of the master curve) around $T \cdot \ln(\frac{t}{\tau_0}) = 150$ K, which corresponds to a blocking temperature of around 5 K. Recalling that, for the reasons discussed in section 3, our size determinations may be slightly underestimated, we conclude from the magnetic measurements that the distribution of particle sizes is peaked around a sphere diameter of 3.7 nm (inflection point of the $T \cdot \ln(t)$ curve), and starts to decrease significantly in the region around 4.3 nm (viscosity saturation above 8 K) to 5 nm (ZFC broad peak around 13 K). This is indeed in good agreement with the data from electron microscopy (Sect. 2).

6. Conclusion

We have studied the low-temperature dynamics of a system of small ($\sim 4$ nm) ferrimagnetic particles of $\gamma$-Fe$_2$O$_3$, in the 0.6 to 12 K range. Beyond the usual plot of the magnetic viscosity versus temperature, which implicitly assumes that the distribution of particle sizes is flat over a range of volumes as large as that of the explored temperatures, we have analyzed the data
with the help of a scaling plot inspired from the spin-glass literature [22, 23]. As a function of the natural variable \( T \cdot \ln(\frac{1}{T_0}) \), which is a measurement of the main energy barrier crossed by thermally activated processes at temperature \( T \) after a time \( t \), all relaxation curves at all temperatures form a unique master curve, whose slope is simply proportional to the barrier distribution. Whatever the exact shape of this distribution, the continuity of the curve ensures that the observed dynamics is thermally activated. In such a plot, crossing of barriers by quasimacroscopic quantum tunneling would appear as a split of the left-hand part (low-temperature) of the curve in small segments, which would have a larger slope than imposed by continuity. Within our experimental accuracy, no such effect can be evidenced. Indeed, according to [4], we can estimate the cross-over temperature \( T_c \) at which the rate of quantum tunneling events should be of the same order of magnitude as thermally activated processes:

\[
T_c = \frac{3\hbar \gamma \sqrt{K_A K_A'}}{2}, \tag{11}
\]

where \( \gamma \) is the gyromagnetic ratio and \( K_A \simeq 8 \times 10^5 \) erg/cm\(^3\) is the anisotropy energy which inhibits the reversal of the particle magnetization ("longitudinal anisotropy"). \( K_A' \) is the "transverse" anisotropy; on account of the cubic symmetry of Fe compounds, it can be expected to be of the same order of magnitude as \( K_A \). This yields \( T_c \sim 0.1 \) K, i.e. at or beyond the limit of the lowest temperatures explored here.

In real macroscopic samples, even carefully prepared, a wide distribution of anisotropy barriers seems to be unavoidable, due to many different dispersion factors such as size, easy-axis orientation, shape etc... Correctly accounting for this unknown distribution is one of the important difficulties encountered in the experiments which aim to evidence for quantum tunneling effects in the magnetization reversal of small particles. The scaling plot presented here helps to handle this difficulty, and in addition gives some information on the distribution. It should be interesting to confirm with this kind of data analysis the present evidences of quantum tunneling phenomena from viscosity measurements of small magnetic particles.

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Note added in proof:

After this work was completed, we learnt that another paper (A. Labarta et al., Phys. Rev. B48 (1993) 10240) also emphasizes the use of a \( T \cdot \ln \frac{T}{t} \) plot for this kind of experiments. We recall that the method which we propose here allows the discrimination between thermal and quantum dynamics without any assumption concerning the barrier distribution. Provided that reliable and systematic measurements of the total magnetization have been done at all temperatures, the crucial test simply consists in checking the continuity of the \( T \cdot \ln t \) curve.
References