Observation of an unusual equilibrium in the molecular nano-magnet Fe\(_8\)

V. Villar,  E. Lhotel,  C. Sangregorio, and C. Paulsen

1Centre de Recherches sur les Très Basses Températures, laboratoire associé à l’Université Joseph Fourier, CNRS, BP 166, 38042 Grenoble cedex 9, France

2INSTM RU and Department of Chemistry, University of Firenze, Via della Lastruccia 3, 50019 Sesto Fiorentino, Italy

Magnetization measurements made in small fields as a function of temperature reveal an unusual equilibrium below 900 mK for the molecular nano-magnet Fe\(_8\). Measurements of the relaxation of the magnetization demonstrate that the approach to the equilibrium is non-trivial and suggest that a competition exists between quantum tunneling of the giant spins and thermodynamic behavior. As a result, at very low temperature the entropy of the spin system remains very large.

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A great deal of interest has been devoted to the study of molecular nano-magnets \(^1\). One of the most prominent examples is the octanuclear iron cluster Fe\(_8\), formula (Fe\(_8\)(C\(_6\)H\(_3\)N\(_3\))\(_6\)(OH)\(_{12}\)Br\(_7\)H\(_2\)O)Br\(_2\)H\(_2\)O which crystallizes in the triclinic P1 system. At low enough temperature, a crystal of Fe\(_8\) can be considered as an ensemble of identical, spin \(S = 10\) nano-magnets with an ising like anisotropy and an easy plane for the reversal of the spin. Spectacular effects have been observed such as temperature independent quantum tunneling of the magnetization with non-exponential decay \(^2\), measurements of the distribution of dipolar fields, hole digging in the distributions and the dependence of hyperfine fields \(^3, 4, 5\), and the observation of the Berry phase \(^6\).

The spin Hamiltonian for Fe\(_8\) with field applied along the easy axis is to a good approximation given by

\[
\mathcal{H} = DS_z^2 + E(S_x^2 - S_y^2) + g\mu_B S_z H. \tag{1}
\]

The last term is the Zeeman energy. The axial and in plane anisotropies, \(D = -0.29\) K and \(E = -0.046\) K have been measured by EPR spectroscopy \(^7\) and other experimental techniques \(^8\). The Hamiltonian describes an energy level schema with \(2S + 1 = 21\) levels. The low lying levels \(m = 10, 9\) etc. are more or less distinct, but mixing do to the off diagonal terms smears out the upper levels \(m < 6\) \(^7\). Above 2 K Fe\(_8\) behaves as a superparamagnet and the relaxation is dominated by thermal activation over an energy barrier given by \(DS_z^2 = 29\) K. Below approximately 360 mK relaxation takes place by temperature independent resonant tunneling between the lowest lying \(m = \pm 10\) levels. The tunnel splitting for the ground state is very small \(\Delta \approx 10^{-7}\) K (10\(^{-2}\) gauss) \(^8\). However the resonance is significantly broadened by internal dipole fields (width at half maximum is of the order of 400 gauss for the unpolarized state) \(^3, 4\) and in addition relaxation by tunneling is aided by (rather slow) nuclear fluctuations which can bring spins that are near resonance into resonance \(^3, 10, 11\). At intermediate temperatures thermally activated quantum tunneling occurs. However, the tunnel splitting for \(m = 6\) or 5 is very large, which opens broad channels in the barrier. As the relaxation times for thermal activation over the barrier become longer, tunneling through these channels becomes more likely which effectively reduces the height of the energy barrier. This in turn will reduce the susceptibility, and reduce relaxation times.

In this letter we report the observation of a plateau in the dc magnetization \(M\) as a function of temperature which occurs below approximately 0.9 K when measured in small fields. This simple observation has been more or less overlooked in the literature, where most of the excitement has focused on the unusual effects at lower temperature. At first glance, it may seem natural to have a plateau when cooling. After all, relaxation times are increasing, and below 1 K become comparable to the characteristic times of most experiments. When cooling too fast, one turns the corner so to speak, and the system becomes frozen in a non-equilibrium state. We will demonstrate below, that the plateau is not an artifact of the cooling rate, and is in fact a new kind of equilibrium.

All measurements were made using low temperature SQUID magnetometers developed at the CRTBT/CNRS. They are equipped with miniature dilution refrigerators that can reach temperatures down to about 0.08 K. Absolute values of the susceptibility and magnetization are made by the extraction method. A number of different single crystals (mass approximately 1 mg) were measured. The samples were aligned with the easy axis along the field.

Figure \(^9\) shows a plot of the field-cooled (and warmed) dc magnetization vs. temperature. The cooling and warming rates were approximately 0.2 K/hour and the measurements were made in an applied field of 25 Oe. At these temperatures 25 Oe may be considered a small field because the magnetization is still linear with field and far from the saturation value \(M_{sat} = 49.5\) emu/gram corresponding to 20 \(\mu_B\) per molecule. Also shown is the real part of the ac magnetization measured at a frequency of 0.001 Hz. Below 0.9 K the magnetization becomes independent of the temperature and a plateau is observed.
FIG. 1: (left) M vs. T measured in a field of 25 Oe applied along the easy axis of a single crystal of Fe$_8$. The cooling rate was approximately 0.2 K/hr. Also shown is an ac magnetization curve for $f = 0.001$ Hz. The dashed line is an extrapolation of the high temperature Curie-Weiss behavior. Below 0.9 K a plateau in the magnetization is observed which appears to be an equilibrium state. The vertical lines show the relaxation of the magnetization toward the plateau (made at constant temperature and 25 Oe field) after first saturating the sample in a large positive field ($a = 0.7$ K and $b = 0.8$ K) or in a large negative field ($c = 0.75$ K and $d = 0.9$ K). (right) The same relaxation data vs. log time indicate that the relaxation follows a simple thermal activation law $\tau = \tau_0 \exp E_b/kT$ over an energy barrier $E_b$. The dashed line is a fit using the high temperature EPR value for $E_b = 29$ K.

In addition, the value of M/H on the plateau is nearly constant for $H < 250$ Oe, i.e. for fields within the first dipole broadened resonance.

The dashed line shown in the figure is an extrapolation of the high temperature Curie-Weiss behavior and deserves some comment. The extrapolation was made by plotting $1/\chi$ and using the restricted temperature range from approximately 2 to 6 K (a slight correction for demagnetization effects was also made). In this temperature range the $1/\chi$ data fall on a straight line and is in good agreement with the $S = 10$ ground state and an enhanced susceptibility due to the rather large Ising like anisotropy of the Hamiltonian [12]. The intercept of the $1/\chi$ plot gives a small positive Curie-Weiss constant <0.1 K, however the extrapolation is quite long, leading to large uncertainty ($\pm 0.1$) in this value. Nevertheless it does indicate that interactions if present, are weak when compared to 1 K. The departure from the Curie-Weiss behavior as the temperature is decreased below 2 K is due to growing importance of thermally activated tunneling.

It is well known that relaxation times $\tau$ for this superparamagnetic system become very long as the temperature is decreased. In figure 2 a plot of $\ln \tau$ vs $1/T$ shows the temperature dependence of $\tau$ measured in two different applied magnetic fields: 25 Oe close to the first resonance, and 850 Oe which is roughly between the first and second resonance. A straight line on this plot would indicate that the relaxation follows a simple thermal activation law $\tau = \tau_0 \exp E_b/kT$ over an energy barrier $E_b$. The dashed line is a fit using the high temperature EPR value for $E_b = 29$ K.

The low temperature data points ($T < 1.4$ K) of figure 2 were made by fitting dc relaxation curves to a single exponential function [13]. The high temperature data points of figure 2 ($T > 0.9$ K) have been determined from the peaks in the imaginary part of the ac susceptibility $\chi''$. The inset shows a typical plot of $\chi''$ vs. log frequency made at fixed temperature $T = 1.4$ K. Note that the curve is not symmetric but has a high frequency shoulder. The dotted line is a fit to the data using the low frequency side of the peak only and assuming the Casimir and du Pré equation $\chi'' \sim \omega \tau / 1 + \omega^2 \tau^2$.

The conclusions that can be drawn from figure 2 and the above analysis is that at least experimentally, relaxation times for Fe$_8$ are well characterized. So is the appearance of the plateau below 0.9 K because the sample was cooled too fast? Consider the following experimental observations which indicate that the plateau is an equilibrium state of the system:

1. The plateau is independent of the cooling rate over a very large range of rates. For example, cooling the sample from 1.5 K to 0.5 K at a relatively fast rate of 1 K per hour or cooling as slow as 1 K over 3 days results in the same plateau.

2. The sample can be slowly cooled to some temperature on the plateau, for example 800 mK, and then monitored at this temperature for days. The magnetization remains
constant. Note that at this temperature and for \( H = 25 \) Oe, we estimate \( \tau \) from figure 2 to be less than 6 hours, much shorter than our experimental time scale.

If the plateau is an equilibrium state, then it is interesting to see how the system moves toward this state when it is out of equilibrium. This can be done in the following ways:

3. By applying a field greater than a few teslas, the sample can be saturated. Then at some fixed temperature below 0.9 K, the magnetic field can be abruptly changed to the value of the given field cooled magnetization, and the magnetization can be measured to see how the system relaxes from above, toward the plateau. Figure 1 (curves a and b) and figure 3 show some typical plots of the relaxation of the magnetization in 25 Oe applied field and at various temperatures using this procedure. As can be seen, the magnetization decreases, approaches and then actually overshoots the plateau, before reversing and approaching the plateau slowly. The relaxation is non-monotonic!

4. Alternatively, the sample can be saturated in a large negative field. Then as above, the field can be rapidly changed to 25 Oe and the ensuing relaxation recorded, this time starting from below the plateau. Two typical curves (c and d) are shown in figure 1. The magnetization comes from below, relaxes upward, and overshoots the plateau, only to turn around, and approach the plateau slowly. Note however, for this measuring field, the overshoot coming from below was less flagrant than from above. A variation on this approach is to rapidly field cool the sample (< 1 second) in the 25 Oe field to some temperature below 0.9 K and watch how it relaxes toward the plateau from below. Many curves have been measured using this technique and the results are essentially the same as above.

5. The above effects can be destroyed and replaced by simple super-paramagnetic behavior if tunneling between the lowest lying states is suppressed. One way that this can be achieved is by applying a magnetic field along the easy axis that lies in between the first resonance at \( H = 0 \) and the second resonance (\( M_z = -10 \) to \( M_z = +9 \)) at \( H = 2000 \) Oe. Thus the left hand side of figure 4 shows the field cooled (0.4 K/hr) magnetization measured in an applied field of \( H = 850 \) Oe. Note that this is a relatively large magnetic field at these temperatures and \( M \) vs. \( H \) is no longer linear.

![FIG. 3: Relaxation of the magnetization vs. time measured in an applied field of 25 Oe and at various constant temperatures. (from left to right) \( T = 0.9, 0.8, 0.75, 0.7, 0.65, 0.6, 0.5 \text{ and } 0.3 \text{ K}. \) The sample was first saturated in a high field.](image)

![FIG. 4: (left) Magnetization vs. temperature "off resonance" for a cooling rate of approximately 0.4 K/hr and measured in a field of 850 Oe. The dashed line is an extrapolation of the high temperature Curie-Weiss behavior. For this cooling rate a plateau in the magnetization is observed below 0.75 K. The vertical lines show the relaxation of the magnetization at constant temperature and in the same 850 Oe field after first saturating the sample in a large positive field (a, 0.85 K) and after rapid field cooling the sample from \( T > 1.5 \) K (\( b = 0.85 \) K and \( c = 0.9 \) K). Note that the magnetization relaxes to a value much higher than that of the plateau and approaches the extrapolated Curie-Weiss value. (right) The same relaxation data plotted as a function of time showing the approach to equilibrium with no over-shoot.](image)
right hand side of the figure plotted as a function of time. The curves are monotonic, there is no overshoot and in fact can be well approximated to a single exponential relaxation. Most important however is that after waiting a long enough time the curves converge to the extrapolated low temperature thermodynamic magnetization.

From these experimental observations we conclude that the plateau, when measured in a small field as in figure 11 represents an unusual equilibrium state of the system, and is clearly not the result one would expect from simple application of the partition function using Eq. 1. The plateau could be the signature of the onset of an ordered state. However in our opinion, at least near 0.9 K, it results from the competition between thermal activation which tends to order the system, and the disorder that results from “indiscriminate” resonant quantum tunneling between the lowest lying states. A simple outline of this process is as follows: in the small applied field of figures 4 and 7 the magnetization value on the plateau $M = \mu_B (n_\uparrow - n_\downarrow)$ represents about a 2.4% excess in the populations of up spins $n_\uparrow$ with respect to down spins $n_\downarrow$ (considering the approximation of a two level system where the total number of spins is given by $n = n_\uparrow + n_\downarrow$). As the temperature decreases, down spins will tend to align with the field direction in order to reduce the free energy and give rise to super paramagnetic behavior $\chi = C/T$. Now imagine a down spin that is in a positive local field $H_{\text{local}}$. If $H_{\text{local}} \gg \Delta$, then relaxation by resonant tunneling is ruled out. This spin can nevertheless flip and align with the local field by thermally activated (non-resonant) tunneling. The temperature and field dependent relaxation time $\tau(T, H_{\text{local}})$ will lie between the two extremal curves given in figure 2. For example $10^{-3} < \tau < 10^{-5}$ sec for $T = 0.8$ K, well within our experimental waiting times.

When this spin flips, it will change the local field of its neighbors, increasing the field on some, decreasing on others, but in particular it will move some spins into resonance or at least close enough to resonance for nuclear fluctuations to become important and thus enabling tunneling between the $m = \pm 10$ states. However this tunneling does not discriminate between up and down spins (after all for these spins $|H| \sim \Delta \simeq 0$). On the other hand, statistically there will be more up spins than down spins, so the probability that an up spin flips down is more likely, and thus the tunneling tends to decrease the magnetization $M$. After a spin has tunneled, it will also change the local field of its neighbors, moving new spins on and off resonance. The process continues by a slow diffusion of tunneling spins through out the sample, and gives rise to a constant rearrangement of up and down spins.

In our model, as the temperature deceases, the entropy of the spins remains very large. For small applied fields as in our experiments, $n_\uparrow \sim n_\downarrow$, and $S \lesssim Nk_B \ln 2$. This should be compared to superparamagnetic behavior were spins align with the field and $S = 0$ at $T = 0$. Implicit in the calculation of the spin entropy is that all configurations of the spin phase space are accessible and are “visited” during some characteristic time $\tau$ which may be very long but finite. As $T \to 0$, one might expect nuclear spins to order or at least freeze out. This would change significantly the tunneling dynamics by eliminating the nuclear fluctuations. Tunneling may continue, but at a reduced rate.

Recently, more experiments have been made which shed additional light on this curious behavior and will be reported elsewhere 11. In particular a transverse field was added to one of the magnetometers. By applying an appropriate transverse field along the hard axis tunneling can be greatly suppressed (a manifestation of the Berry phase for nano-magnets) 8, 15. When tunneling is suppressed by this method, the results are similar to point 5: super-paramagnetic behavior is restored and the plateau depends on cooling rate. This further reinforces the idea that tunneling is responsible for the plateau.

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