Nonexponential Dynamic Scaling of the Magnetization Relaxation in Mn_{12} Acetate

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We present new results on the zero-field magnetic relaxation in a single crystal of Mn_{12} acetate. We find three relaxation regimes. Above 2.8 K, the relaxation is exponential. Below this temperature, deviations are observed. These deviations are more pronounced when temperature decreases between 2.4 and 2.0 K. Below 2.0 K they lead to a square root relaxation. A scaling analysis is proposed, which shows the dipolar interactions can be treated as a time-dependent local mean field in the thermally activated tunneling regime. These evolutions of local mean field produce deviations from the exponential relaxation and can explain the square root regime at lower temperature.

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The observation of quantum phenomena at the mesoscopic scale is a challenging problem in condensed matter physics [1]. In magnetism, this field of research has been particularly active in the last few years [2]. Striking evidence for quantum tunneling of the magnetization has been found in the organometallic compounds Mn_{12} acetate (Mn_{12}-ac) [3–6] and then in Fe_8 [7]. Hysteresis studies performed on a single crystal of Mn_{12}-ac [6] have shown unusual staircaselike loops, with field-periodic magnetization steps. These steps occurred at the crossing of the level scheme of the spin $S = 10$ of a molecule. Theoretical investigations have shown that quantum tunneling of a single $S = 10$ molecule can account neither for the number of steps nor for their magnitude [8]. These discrepancies suggest that the coupling to the environment plays a crucial role in the tunneling phenomena of Mn_{12}-ac molecules.

In this Letter, we report new results concerning zero-field magnetic relaxation. Even if tunneling is essentially a single molecule process, we find that the relaxation law *M*(*t*) deviates strongly from exponential, even at relatively high temperature, as a consequence of intermolecular dipolar couplings. Above 2 K, deviations from an exponential time decay occur because the dipolar field distribution evolves during the magnetization relaxation. Dipolar interactions act as a time dependent local mean field, while the relaxation time follows the Arrhenius law. Below 2.0 K, we observe a weaker dependence on the temperature and an unusual square root relaxation law. This result is compared with a recent theoretical model [9] in which tunneling is assisted by fluctuations [6] of nuclear spins and intermolecular dipolar interactions [9].

The relaxation experiments were performed on a parallepipedic single crystal of Mn_{12}-ac, using a conventional SQUID magnetometer, in zero applied field and in the temperature range 1.5–3 K. This single crystal (85 μg weight) was taken from a powder synthesized at the Department of Chemistry, University of Florence. In order to saturate the sample, a magnetic field of 5 T was applied along the easy axis of magnetization of the crystal (from the slope of the magnetization curve, the misorientation was found to be less than 5°). The magnetic field was then reduced to zero at a rate of 1 T per minute, at constant temperature. The delay before starting measurements was about 10 min. The time zero was fixed at the beginning of this stabilization delay. Depending on the temperature, measurements lasted up to 10^5 s.

A set of raw relaxation data is plotted in a semilogarithmic scale in Fig. 1 (top part for $1.5 < T < 2.1$ K and bottom part for $2.2 < T < 2.7$ K). While such curves

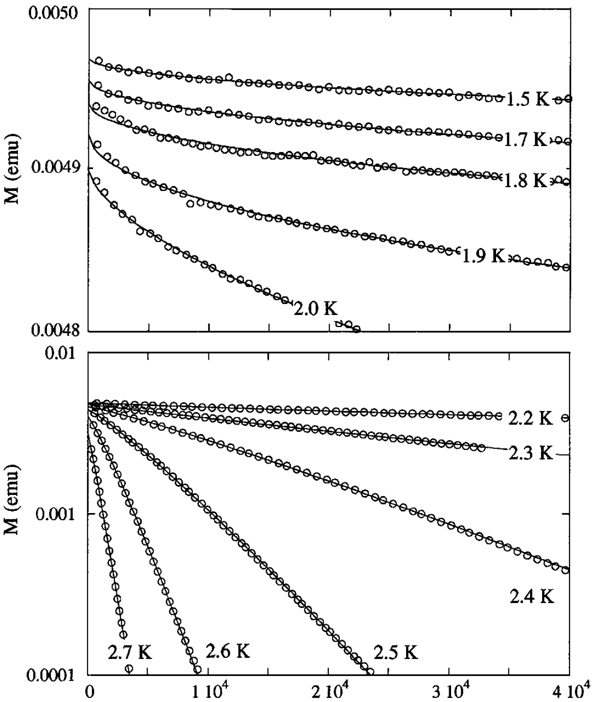

FIG. 1. Time decay of the magnetization, measured in the remanent state at different temperatures. Note that the magnetization decay, plotted in logarithmic scale, is in general nonexponential. Lines show the fit of the data points to a stretched exponential function.

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have often been fitted with an exponential, it is obvious that this law does not describe the measurements in the whole range of temperature and time properly. The fits are often restricted to the long-time tail of the relaxation curves. This limits the analysis to a small fraction of the magnetization decay [10]. In order to achieve a good fitting of the data in the whole experimental range of time and temperature, it is then necessary to go beyond this relaxation law. As shown in Fig. 1 (continuous lines), the stretched exponential law $M = M_0 \exp[-(t/\tau)^{\beta}]$ gives a better agreement ($M_{\text{initial}} = M_0$ and $M_{\text{equilibrium}} = 0$). Using this expression, the data can be fitted reasonably in the main part of our experimental time range. As a consequence of these fits with two free parameters the mean relaxation time τ and β, the uncertainty on the values of β is significant, particularly when the magnetization decay is small in the experimental time range (below 2.0 K, β is defined with an accuracy of ± 0.2). However, it is found that β is strongly temperature dependent. Below 2.0 K, β is approximately constant and close to 0.5, given the large uncertainty on the fitting parameters at these temperatures. It increases linearly with temperature up to 2.4 K to reach $\beta = 1.1$, and then it slightly decreases at higher temperatures (between 2.8 K and the blocking temperature $T_B = 3$ K, $\beta = 1$). The mean relaxation time τ starts to follow the Arrhenius law $\tau = \tau_0 \exp(E/T)$ roughly above 2 K with the attempt time $\tau_0 \approx 10^{-7}$ s and the energy barrier $E = 61(\pm 1)$ K, as previously reported [3–6]. Below 1.9 K, the large uncertainty on the exponent β induces some scattering on the fitted characteristic time. However, with a fixed value $\beta = 0.5$, τ is weakly dependent on the temperature below 1.9 K and tends towards $\tau(1.5\ \text{K}) = 1.5 \times 10^9$ s.

Fitting the data to a stretched exponential law is not really satisfactory, especially at low temperature. This law allows fitting almost any curve, while the theoretical basis for such a fit is lacking. However, this analysis does suggest the existence of two relaxation regimes (i) below 2 K, the mean relaxation time becomes as large as 50 years, and it depends weakly on the temperature and (ii) above 2 K, it becomes faster and follows an Arrhenius law. The time decay of the magnetization is not exponential (except just below T_B), and it depends strongly on the temperature. In what follows, we show that one may analyze these results in a quite different way, allowing for a better understanding of these two relaxation regimes.

In the low temperature regime, below 2 K, where $\beta = 0.5$ and $t/\tau \ll 1$, the magnetization relaxation can in fact be well described by a square-root law, $M_0[1 - (t/\tau)^{1/2}]$. As shown in Fig. 2, where the data are plotted as a function of $t^{1/2}$, this simple law fits the experiments very well up to 1.7 K, while the discrepancy progressively increases at higher temperatures. One should notice that the extrapolated zero-time magnetization depends on the temperature. This offset is too big to be related solely to the shift on the clock time-zero (of the order of 500 s). This suggests that a small fraction of the total magnetization relaxes faster at short times, before the magnetization begins to be recorded [11]. However, this contribution is unlikely to be relevant to our experimental time and temperature range [12].

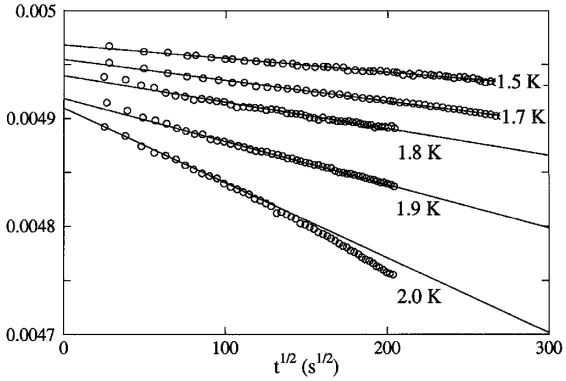

FIG. 2. Time decay of the remanent magnetization measured at low temperature, plotted as a function of the square root of the time. Lines show linear fits.

Such a square-root relaxation was recently proposed in a theoretical model for an assembly of nanomolecules with dipolar and hyperfine interactions [9]. This model is in principle valid at zero temperature and short times, when initial M is close to the saturation magnetization M_s. It predicts that the square-root decay arises from the formation of a nonequilibrium depletion in the dipolar field distribution, at the tunnel energy [13]. In the present experiments in Mn_{12}-ac, the distribution of dipolar fields is nearly at equilibrium (at the time scale of experiments), but it follows the slow shift of its mean value with time (leading to a change in the density of dipolar field states, responsible for nonexponential decay). Our experimental observation of a square-root relaxation at low but finite temperature, when the system is close to saturation, supports this picture. In this regime, the characteristic time τ is found to be weakly dependent on temperature (cf. Fig. 3). It varies between 10^8 and 1.5×10^9 s between 1.9 and 1.5 K.

In the high temperature regime ($T > 2.0$ K), we find that, quite remarkably, the data fit a single scaling function, $f(t/\tau(T))$. The master function $f(x)$ is such that $f(0) = M_s$ and $f(\infty) = 0$, and $\tau(T)$ is the relaxation time. All the data points of isotherms measured between 2.0 and 2.8 K are scaled on the curve measured at 2.0 K, using the transformation $t_{\text{sc}} = (t + t_w)\tau(2.0)/\tau(T)$. This leads to the scaling plot of $M(t)$ versus t_{sc} shown in Fig. 4. The translations $t_w(T)$ are of the order of the field stabilization delay (500 s). This scaling analysis allows us to extract the mean relaxation time $\tau(T)$. Note that thanks to this scaling analysis $\tau(T)$ is determined without making any assumption about the relaxation law. In this range of temperature, $\tau(T)$ follows the Arrhenius law, with the same

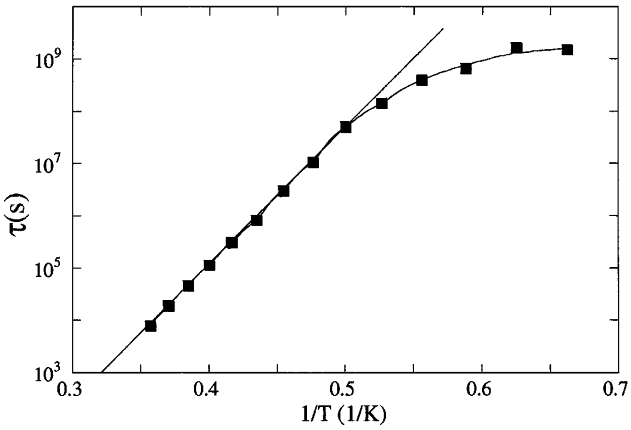

FIG. 3. Semilogarithmic plot of the characteristic time. The line between points is only a guide for the eye. The straight line is the Arrhenius fit of the high temperature regime.

parameters as found above (cf. Fig. 3). As shown in Fig. 4, the master curve is not exponential. Strong deviations from this behavior (for $t_{\mathrm{sc}} < 10^6$) can be understood as a consequence of dipolar interactions. During the measurement, the magnetization and the mean dipolar field evolve (in the Lorentz mean field framework, the local field is simply proportional to the magnetization per volume). As the relaxation rate is strongly field dependent near a tunnel resonance [6], it must vary during the measurement. This explains the $\beta \neq 1$ values found above in the stretched exponential analysis. In fact, the exponential time decay is observed only when the magnetization variations are small in the experimental time scale (e.g., above 2.8 K, where $\beta \approx 1$, about 90% of the total magnetization has already relaxed before we started recording the data). One important consequence of the observed scaling is that the relaxation does not depend on magnetic history above 2.0 K, showing that there are no memory effects associated with multimolecular correlations, in this regime. However, as shown by the deviations from exponential decay, observed even in the thermally activated regime, quantum relaxation in Mn_{12}-ac is not a single molecule process.

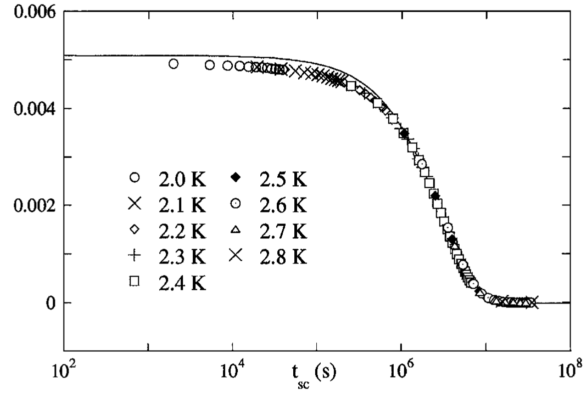

FIG. 4. Scaling plot of relaxation data, measured at nine different temperatures, between 2.0 and 2.8 K. For clarity, only about 5% of the data points have been plotted. The continuous line shows the fit of the master curve to an exponential function.

In conclusion, this study of the quantum relaxation measured in zero field on a single crystal of Mn_{12}-ac shows the existence of two regimes. In both regimes, the relaxation is not exponential, because of the existence of dipolar interactions (except just below T_B). Above 2.0 K, we find a scaling of the relaxation curves, showing that dipolar interactions act essentially as a time (and temperature) dependent mean field. The mean relaxation time $\tau(T)$ starts to follow the Arrhenius law at about 2 K. At lower temperatures, a square-root relaxation law is measured, with a weak temperature dependence of the characteristic time. Such a behavior has been recently predicted in a model by Prokof'ev and Stamp [9]. The comparison between experiment and theory suggests the following scenario. At high temperatures, both phonon induced crystal field [15,16], longitudinal hyperfine and dipolar fluctuations [17] are fast enough [9] to repopulate continuously the energy levels, keeping the density of states available for tunneling in equilibrium value. Thus, multimolecular correlations in dipolar field distributions, induced by activated tunneling, play a negligible role and the observed deviations from exponential relaxation come only from the time evolution of the local mean field (Lorentz and demagnetizing field). On the contrary, at low enough temperatures, when crystal field and dipolar fluctuations are frozen, the molecular spin system is no longer in equilibrium and the relaxation, induced by nuclear spin fluctuations, takes the square-root form of Ref. [9].

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