Relaxation of muon spins in molecular nanomagnets

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We address the cause of the unusual muon spin-relaxation (μSR) results on molecular nanomagnets (MNMs). Through measurements on protonated and deuterated samples of the MNMs Cr7Mn (S=1) and Cr8 (S=0), we show that the muon spin for S ≠ 0 MNMs is relaxed via dynamic fluctuations of the electronic spins. A freezing out of dynamic processes occurs on cooling and at low temperatures the muon spins are relaxed by the electronic spins which themselves are dephased by incoherent nuclear-field fluctuations. We observe a transition to a state of static magnetic order of the MNM electronic spins in Cr7Mn below 2 K.

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Molecular nanomagnets (MNMs) (Ref. 1) comprise clusters of exchange-coupled transition-metal ions which often have a negative anisotropy constant favoring a ground state with a large eigenvalue of the electronic spin component Sz. These systems have been widely studied in recent years, most recently in anticipation of their deployment as elements of quantum computers2,3 although much interest also centers on the quantum tunnelling of the magnetization (QTM) which takes place when the magnetic energy levels are at resonance.1 A theory of QTM is based on the Landau-Zener paradigm4 of energy levels brought into resonance by a time-dependent field. The precise details of the mechanism for QTM in MNMs remain unresolved and while pairwise dipole interactions between spins are certainly important5 a promising suggestion is that resonance is achieved as a result of the stochastically varying magnetic field B(t), which arises from the incoherent fluctuations of nuclear moments surrounding the transition-metal ions6 (a typical MNM contains ~106 protons due to the organic ligands).

MNMs have been successfully probed using techniques such as magnetization,7 heat capacity,8 neutron scattering,2,10 and electron spin resonance (ESR).3 In contrast, measurements made using muon spin relaxation (μSR) have proven difficult to interpret. Although initially it was thought that QTM should be measurable by implanting muons into MNMs,9,11–13 the unambiguous detection of this effect proved elusive.14 Instead, μSR spectra obtained on high spin systems appeared to arise from dynamic fluctuations of a local magnetic field distribution at the muon sites, which persisted down to dilution refrigerator temperatures.12–14 Muon results on MNM systems all showed similar behavior14 but it was unclear whether the muon was probing the intrinsic behavior of the large electronic spin or some residual effect. It was argued recently by Keren et al.15 that μSR is sensitive to the relaxation of the MNM electronic spins caused by the incoherent fluctuations of nuclear moments surrounding the metal ions. If this is the case then it makes the muon a valuable probe of the potential mechanism behind QTM. In order to address the question of what the muon probes in MNM systems we have made identical μSR measurements on protonated and deuterated samples of Cr7Mn (S=1) and Cr8 (S=0) (Refs. 16–19) (structure shown in Fig. 1). We show (i) that the muon is controlled by the large electronic spin in an MNM; (ii) deuteration leads to a significant increase in the μSR relaxation rate at low temperature in Cr7Mn, implying that muons probe the relaxation of large electronic spins by the random magnetic fields due to the nuclei, and (iii) that upon cooling, a magnetic ground state is reached by a freezing out of dynamic processes that leads to magnetic order in Cr7Mn below 2 K.

In a μSR experiment20 spin-polarized positive muons are stopped in a target sample. The time evolution of the muon spin polarization is probed via the positron decay asymmetry function A(t) to which it is proportional. Our μSR measurements were made on the ARGUS instrument at the RIKEN-RAL facility, ISIS, Rutherford Appleton Laboratory, U.K. and on the low temperature facility (LTF) and general purpose spectrometer (GPS) instruments at the Swiss Muon Source (SμS), Paul Scherrer Institut, CH. Powder samples of the materials were packed in Ag foil and mounted on a Ag backing plate in 3He and 4He cryostats. Typical spectra measured for Cr7Mn and Cr8 are shown in Fig. 1. Above T= 2 K the spectra for all materials differ depending on whether protonated or deuterated (Fig. 1).

To compare the Cr7Mn and Cr8 systems, measurements were made over the temperature range 2 ≤ T ≤ 100 K. In this regime the spectra for S=1 Cr7Mn [Fig. 1(a)] were found to be described by the relaxation function A(t)=A1 exp(−λt) + Abg, where Abg accounts for any background contribution from muons that stop in the sample holder or cryostat tails. This behavior is typical of that observed previously in MNM materials12,13,15 and arises because of the complex dynamic distribution of local fields within the material sampled by the muon ensemble. The monotonic relaxation and the fact that the muons could not be decoupled with an applied magnetic field up to 0.6 T places the relaxation in the fast-fluctuation limit.21

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The spectra measured for the $S=0$ Cr$_8$ samples are quite different [Fig. 1(b)]. In this case the relaxation rate is far smaller and resembles a Kubo-Toyabe (KT) function $f_{KT}(\Delta)$ with $\Delta = \gamma_B(B_0 - B)^2$ where $\gamma_B = 2\pi \times 135.5$ MHz T$^{-1}$ is the muon gyromagnetic ratio and $B$ is the local magnetic field at a muon site. However, the KT function, which describes relaxation due to static random magnetic fields at the muon sites, could not adequately describe all of the data. This is probably to be expected in a complex material such as a MNM where many inequivalent classes of muon sites occur and lead to a distribution of second moments $p(\Delta)$. The resulting muon relaxation is obtained by averaging the KT function over this distribution. For simplicity we modeled the relaxation by taking $p(\Delta)$ to be a uniform distribution up to a maximum $\Delta_0$. One this one-parameter model successfully fitted the data for both materials over the entire range. The fitted values of $\Delta_0$ are shown in Fig. 2(a) and are quite $T$ independent and take average values $\Delta_0 = 0.56(1)$ MHz for Cr$_8$-h and $0.48(1)$ MHz for Cr$_8$-d. Our conclusion from these measurements is that the muon is sensitive to the disordered nuclear moments in Cr$_8$. This is confirmed by the application of a small longitudinal magnetic field which quenches the relaxation. The larger $\Delta_0$ in Cr$_8$-h compared to Cr$_8$-d reflects (albeit partially) the larger moment of the proton. Most importantly, the dramatic difference between the measured spectra and relaxation rates for $S=0$ Cr$_8$ and $S=1$ Cr$_7$Mn samples (Fig. 1) strongly suggests that the muon response in MNM systems with $S \neq 0$ stems from dynamic fluctuations of the electronic spin. In the absence of an electron spin in Cr$_8$, the muon spin is relaxed by quasistatic disordered nuclear moments.

We now turn to the role of the nuclei in the spin relaxation process in $S=1$ MNMs. The temperature dependence of the relaxation rate $\lambda$ for the protonated ($\lambda^p$) and deuterated ($\lambda^d$) Cr$_7$Mn samples is shown in Fig. 2(a). These measurements were made with a magnetic field of 1 mT applied parallel to the initial muon spin direction which was intended to quench any residual relaxation of the muon spin caused directly by fluctuating nuclear spins as seen in the Cr$_8$ samples. On cooling below $T \approx 50$ K, the relaxation rate $\lambda$ increases before saturating below $\sim 10$ K, with the onset of the increase and the saturation occurring at similar values of $T$ for both materials. This $T$ dependence is common to nearly all MNM systems that have been previously measured with $\mu^+\text{SR}$ (Refs. 12–15) and is discussed in more detail below. At high $T$ we see that $\lambda^d > \lambda^p$. It is likely that at these high temperatures the electronic spins are fluctuating very fast and are at least partially motionally narrowed from the spectra. Upon cooling the increase in $\lambda$ is greater for the deuterated sample, with $\lambda^d$ becoming greater than $\lambda^p$ below $\sim 15$ K. Most significantly the saturation of the relaxation at $T \leq 10$ K occurs with $\lambda^d > \lambda^p$. The $T$ dependence of the ratio $\lambda^d/\lambda^p$ [Fig. 2(b)] which increases on cooling tends to $\sim 1.7$ at the lowest temperature.

The low-temperature results may be understood using the model of $\mu^+\text{SR}$ in MNM systems proposed by Keren et al. Here a muon spin $I$ is coupled to a single MNM electronic spin $S$ and dynamic fluctuations of the local protons cause $S$ to experience a nuclear stochastic field $B_n(t)$, along with any externally applied field $B_0$. This system may be described by the resulting Hamiltonian $H = g_S \mu_B S \cdot \{B_n(t) + h \gamma_B (B_0 + FS)\}$, where $F$ couples the muon and electronic spin. We ignore the direct response of the muon to the stochastic field, which we know to be small from the Cr$_8$ results. The spin relaxation resulting from this model may be simply understood. The magnetic field distribution experienced by a particular spin population is characterized by a correlation function whose Fourier transform (known as the spectral weight) will be proportional to the spin-relaxation rate. We assume that the stochastic magnetic field $B_n(t)$ experienced by the MNM spin due to the nuclei will be described by $\langle B_n(t)B_n(0)\rangle = \langle B_n^2 \rangle \exp(-t/\tau_n)$, where $\tau_n$ is the correlation time of the nuclear stochastic field. A Fourier transform reveals that the nuclear fields will relax the electron spins at a rate $1/\tau_n \ll \langle B_n^2 \rangle \tau_n$. To find the relaxation rate of the muon spin due to the fluctuations of the electronic spins, we again assume that the correlation function takes the form

![Figure 1](image1.png)

**FIG. 1.** (Color online) $\mu^+\text{SR}$ spectra for protonated and deuterated (a) Cr$_7$Mn and (b) Cr$_8$ materials, measured at $T = 4.5$ K. Inset: structures of the molecules.

![Figure 2](image2.png)

**FIG. 2.** (Color online) (a) Temperature evolution of the relaxation rates $\lambda$ for Cr$_7$Mn and $\Delta_n$ for Cr$_8$. The lines are fits to a phenomenological equation (see main text). (b) Ratio of the Cr$_7$Mn-h and -d relaxation rates. The line is a guide to the eye.
(Bµ(t)|Bµ(0))=⟨Bµ2⟩exp(−t/τµ), where Bµ is the effective local field at the muon site due to the large spin S and τµ is the correlation time for the electronic spins. Taking a further Fourier transform gives the µ-SR relaxation rate \[ R(t) = \gamma_0^2(B_0^2)\tau_\mu \{1 + (\gamma_\mu B_0^2/\tau_\mu)\} \] which in the limit of small applied magnetic fields becomes

\[ \lambda = \gamma_0^2(B_0^2)\tau_\mu \approx \frac{\langle B_\mu^2 \rangle}{\langle B_n^2 \rangle} \frac{1}{\tau_n}. \]

The primary effect of swapping protons for deuterons might be expected to be the factor 3.26 decrease in the size of the nuclear moments experienced by the electronic spin, reducing the second moment of the field distribution due to the electronic spin ⟨B_n^2⟩. There is good evidence for this reduction from ESR (Ref. 3) in the similar system Cr7Ni, where it was found that 1/T2 decreased upon deuteration, demonstrating that the electronic spins are directly relaxed by proton fluctuations. Equation (1) shows that a decrease in ⟨B_n^2⟩ will lead to an increase in the muon relaxation rate λ. The larger magnitude of λ for the Cr7Mn-d sample at all temperatures is therefore consistent with the electronic spin being depolarized by the nuclei. Since the electronic spins, and hence ⟨B_n^2⟩, have the same magnitude in both materials, then we have λd/λn=⟨B_n^2⟩/⟨B_n^2⟩τ_n=⟨B_n^2⟩τ_n. For our systems, we might expect that λd/λn=2/2=11.99. However, this prediction results from considering the Overhauser field in an MNM (Ref. 23), leading to the prediction that λd/λn=3.99. The measured increase at low temperatures is, however, a factor of ~1.7. A discrepancy is not surprising, particularly given that the ratio of measured Δn factors for Cr7Mn-h and -d samples is less than the factor predicted above for the second moments. However, this alone is not enough to explain the size of the discrepancy and this may provide evidence that the reorientations of the electronic moments caused by the nuclei are not isotropic.

Finally, we address the characteristic temperature dependence of λ observed in all S ≠ 0 MNM systems. It is generally found in MNMs (Ref. 14) that on decreasing the temperature from T∼100 K there is an increase in λ with the relaxation rate leveling off to some value λ_sat below ~10 K. This behavior may be explained by involving two competing dynamic relaxation processes, one dominant at high temperatures and described by a strongly temperature-dependent correlation time τ(T) and one, dominant at low temperatures described by a weakly T-dependent correlation time τ_n. In the presence of two competing processes, that with the shorter correlation time dominates, giving the smaller relaxation rate (since λ∝1/T). At high temperature, therefore, we have τ(T) ≤ τ_n which results in a strongly T-dependent relaxation which we can crudely model phenomenologically with λ=C exp(U/T), where U represents an energy barrier. At low temperatures when some of the T-dependent relaxation channels have been frozen out, τ(T) ≤ τ_n and we have λ ~ λ_sat. This behavior results in a phenomenological fitting function 1/λ(T) = 1/λ_sat + 1/[C exp(U/T)] which has been used previously to characterize these MNM systems.14 Fitting this formula to our data [Fig. 2(a)] yields

\[ C^h=0.23(3) \text{ MHz, } U^h=46(4) \text{ K, } \lambda_{sat}^h=2.00(4) \text{ MHz, } C^d=0.070(1) \text{ MHz, } U^d=51(3) \text{ K, and } \lambda_{sat}^d=3.3(1) \text{ MHz}. \]

There is an intriguing similarity between the muon results in MNM systems and those in some inorganic materials, such as Ca_{3}Co_{2}−_{x}Mn_{x}O_{6−y} where the physics involves significant single-ion anisotropy and a complex (often glassy) freezing out of dynamic processes. It is probable that the relaxation of the electronic spins we probe in MNMs is explainable within the same framework. At high temperatures magnetoelastic interactions provide the main relaxation mechanism for the electronic degrees of freedom. Our data show U^h≈U^d since, if the T dependence is due to spin-phonon coupling through the modulation of local crystal fields, this barrier height should only depend on the electronic energy level structure. As the temperature is decreased, some relaxation channels will be frozen out, increasing the correlation time of the electronic moments.25 The low-temperature channel that gives rise to the temperature-independent relaxation λ_i sat seen in µ-SR would appear to be the relaxation of the electronic spins by the nuclear fluctuations, allowing us to identify τ_n with τ(T), the electronic correlation time discussed above. This situation is similar to the electronic T_1 which is dominated by phononic contributions at high temperatures and by nuclear contributions at low temperature.26 This is not the case for the electronic 1/T_1 which is phonon dominated down to ~2 K. This difference between 1/T_1 and 1/T_2 for ESR suggests that the nuclei contribute to the secular part of the relaxation, that is, the relaxation of the electron spins due to a spread in the net magnetic field at the spin sites.3,22

In order to further probe the freezing out of the dynamics in Cr7Mn, measurements were made down to 20 mK using the LTF instrument at SPS. At the lowest temperatures heavily damped oscillations are observed at early times (Fig. 3) in both Cr7Mn-h and -d. Oscillations are usually caused in muon spectra by quasistatic magnetic order, causing a coherent precession of muon spins. The observed oscillations show little temperature dependence in the range 0.02≤T≤1 K and are identical for -h and -d samples. For measurements made in the same temperature range at ISIS, oscillations are not discernible due to the resolution limit set by the ISIS muon pulse width. However, the spectra do show a discontinuous change around T=2 K (inset Fig. 3) with a
loss of initial asymmetry and a sharp increase in the apparent relaxation rate observed below this temperature. There is also significant magnetic hysteresis on the application and removal of applied magnetic fields below 2 K. From these measurements we estimate that a transition to a state of static magnetic order takes place at $T = 1.9(1)$ K. The heavily damped nature of the oscillations and the $\text{Cr}_8$ results suggest that there are many magnetically inequivalent muon sites in the system. The results demonstrate that the intermolecular exchange $J$ is nonzero in the $S=1$ system and, using mean-field theory\textsuperscript{27} (assuming $z=6$ nearest neighbors) we estimate $J/k_B = 3T_C/2zS(S+1) = 0.2$ K.

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\textsuperscript{1} D. Gatteschi, R. Sessoli, and J. Villain, \textit{Molecular Nanomagnets} (Oxford University Press, New York, 2006).
\textsuperscript{2} M. N. Leuenberger and D. Loss, \textit{Nature (London)} \textbf{410}, 789 (2001).
\textsuperscript{3} A. Ardavan, O. Rival, J. J. L. Morton, S. J. Blundell, A. M. Tyryshkin, G. A. Timco, and R. E. P. Winpenny, \textit{Phys. Rev. Lett.} \textbf{98}, 057201 (2007).
\textsuperscript{4} L. D. Landau, \textit{Phys. Z. Sowjetunion} \textbf{2}, 46 (1932); C. Zener, \textit{Proc. R. Soc. London, Ser. A} \textbf{137}, 696 (1932).
\textsuperscript{5} A. Morello, P. C. E. Stamp, and I. S. Tupitsyn, \textit{Phys. Rev. Lett.} \textbf{97}, 207206 (2006).
\textsuperscript{6} N. V. Prokof’ev and P. C. E. Stamp, \textit{Phys. Rev. Lett.} \textbf{80}, 5794 (1998).
\textsuperscript{7} A. Cornia, D. Gatteschi, and R. Sessoli, \textit{Coord. Chem. Rev.} \textbf{219-221}, 573 (2001).
\textsuperscript{8} F. Fominaya, J. Villain, P. Gandit, J. Chaussy, and A. Caneschi, \textit{Phys. Rev. Lett.} \textbf{79}, 1126 (1997).
\textsuperscript{9} M. Hennion, L. Pardi, I. Mirebeau, E. Suard, R. Sessoli, and A. Caneschi, \textit{Phys. Rev. B} \textbf{56}, 8819 (1997).
\textsuperscript{10} R. Caciuffo, T. Guidi, G. Amoretti, S. Carretta, E. Livioiti, P. Santini, C. Mondelli, G. Timco, C. A. Muryn, and R. E. P. Winpenny, \textit{Phys. Rev. B} \textbf{71}, 174407 (2005).
\textsuperscript{11} A. Lascialfari, Z. H. Jang, F. Borsa, P. Carretta, and D. Gatteschi, \textit{Phys. Rev. Lett.} \textbf{81}, 5773 (1998).
\textsuperscript{12} A. Keren, P. Mendels, V. Marvau, A. Scuiller, M. Verduguer, J. S. Lord, and C. Baines, \textit{Phys. Rev. B} \textbf{65}, 132403 (2002).
\textsuperscript{13} J. Blundell \textit{et al.}, \textit{Synth. Met.} \textbf{133-134}, 531 (2003).
\textsuperscript{14} T. Lancaster \textit{et al.}, \textit{J. Phys.: Condens. Matter} \textbf{16}, S4563 (2004).
\textsuperscript{15} A. Keren, O. Shafir, E. Shimshoni, V. Marvau, A. Bachschmidt, and J. Long, \textit{Phys. Rev. Lett.} \textbf{98}, 257204 (2007).
\textsuperscript{16} E. K. Larsen \textit{et al.}, \textit{Angew. Chem. Int. Ed.} \textbf{42}, 101 (2003).
\textsuperscript{17} J. van Slageren \textit{et al.}, \textit{Chem.–Eur. J.} \textbf{8}, 277 (2002).
\textsuperscript{18} S. Piligkos \textit{et al.}, \textit{Chem.–Eur. J.} \textbf{15}, 3152 (2009).
\textsuperscript{19} The full chemical formulae of the materials studied are $\text{Cr}_7\text{Mn}_h\text{F}_8\text{O}_2\text{CC(CH}_3\text{)}_3\text{Cl}_{16}$; $\text{Cr}_2\text{Mn}_d\text{F}_8\text{O}_2\text{CC(CH}_3\text{)}_3\text{Cl}_{16}$; $\text{Cr}_8\text{F}_8\text{O}_2\text{CC(CH}_3\text{)}_3\text{Cl}_{16}$; and $\text{Cr}_8\text{F}_8\text{O}_2\text{CC(CH}_3\text{)}_3\text{Cl}_{16}$.
\textsuperscript{20} S. J. Blundell, \textit{Contemp. Phys.} \textbf{40}, 175 (1999).
\textsuperscript{21} R. S. Hayano, Y. J. Uemura, J. Imazato, N. Nishida, T. Yamazaki, and R. Kubo, \textit{Phys. Rev. B} \textbf{20}, 850 (1979).
\textsuperscript{22} C. P. Slichter, \textit{Principles of Magnetic Resonance} (Springer-Verlag, New York, 1989).
\textsuperscript{23} P. C. E. Stamp and I. S. Tupitsyn, \textit{Phys. Rev. B} \textbf{69}, 014401 (2004).
\textsuperscript{24} T. Lancaster, S. J. Blundell, P. J. Baker, H. J. Lewtas, W. Hayes, F. L. Pratt, H. T. Yi, and S. W. Cheong, \textit{Phys. Rev. B} \textbf{80}, 020409(R) (2009).
\textsuperscript{25} P. Santini, S. Carretta, E. Livioiti, G. Amoretti, P. Carretta, M. Filibian, A. Lascialfari, and E. Micotti, \textit{Phys. Rev. Lett.} \textbf{94}, 077203 (2005).
\textsuperscript{26} E. Troiani, V. Bellini, and M. Affronte, \textit{Phys. Rev. B} \textbf{77}, 054428 (2008).
\textsuperscript{27} S. J. Blundell, \textit{Magnetism in Condensed Matter} (OUP, Oxford, 2001).