

Dynamics at $T \rightarrow 0$ in half-integer isotropic high-spin molecules

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We investigate the dynamical spin-spin autocorrelation function of the isotropic high-spin molecules CrCu_6 ($S=9/2$), CrNi_6 ($S=15/2$), and CrMn_6 ($S=27/2$), using magnetization, spin-lattice relaxation of muon spin (μSR), and NMR measurements. We find that the field autocorrelation time τ of the molecule's spin at zero and low fields is nearly temperature independent as $T \rightarrow 50$ mK. The high temperature τ is very different between the three molecules. Surprisingly, it is identical (~ 10 ns) at low temperature. This suggests that τ is governed by hyperfine interactions.

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High-spin molecules (HSM's) consist of clusters of metal ions, ordered in a crystal lattice, and coupled by Heisenberg ferromagnetic or antiferromagnetic interactions with a coupling constant J , only between spins \vec{S}_i in the molecule. At low temperatures $k_B T \ll |J|$ these spins lie parallel or antiparallel to each other, and the molecule is in its ground spin state, where $\vec{S} = \sum_i \vec{S}_i$ is high, with quantum number S , and $2S+1$ degeneracy. At even lower temperatures, $k_B T \ll J$, the degeneracy can be removed by additional anisotropic interactions such as the uniaxial term DS_z^2 , or rhombic term $E[S_x^2 - S_y^2]$, etc. Experiments on the two most famous high-spin molecules Mn_{12} (Ref. 1) and Fe_8 (Refs. 2 and 3) show that at low T the main interaction is, indeed, the uniaxial anisotropy, where up- and down-spin states $S_z = \pm S = \pm 10$ are degenerate, and tunneling is induced between these states by an additional term in the Hamiltonian that does not commute with S_z . This quantum tunneling of magnetization (QTM) phenomenon has received considerable attention in recent years, focusing mainly on additional terms in the Hamiltonian which are responsible for the tunneling.³⁻⁵ Nevertheless, the theoretical picture is far from being clear and existing models are controversial, and often contradict each other.⁶ In some cases, even qualitative understanding of the observed experimental data is absent.⁷

In this paper we investigate three simple HSM systems, which are isotropic ($D, E = 0$). In these systems no tunneling is observed due to the absence of the uniaxial term DS_z^2 . However, spin dynamics is observed even at very low temperatures ($T = 50$ mK). Therefore, the additional terms in the spin Hamiltonian could be probed directly in these systems. Such a study can highlight the role of phonons,^{6,8} dipolar interactions, and nuclear fluctuations⁵ in a simple setup. In addition, it could serve as a large S limit for isotropic models usually applied only for the $S = 1/2$ case,⁶ or it could serve as a $D \rightarrow 0$ test case for anisotropic HSM models.⁹

We present an experimental investigation using three types of measurements: magnetization, spin-lattice relaxation

(T^{-1}) of muon spin (μSR), and that of proton spin (NMR). Our molecules are $[\text{Cr}\{(\text{CN})\text{Cu}(\text{tren})\}_6](\text{ClO}_4)_{21}$,¹⁰ $[\text{Cr}\{(\text{CN})\text{Ni}(\text{tetren})\}_6](\text{ClO}_4)_9$,^{11,12,10} and $[\text{Cr}\{(\text{CN})\text{Mn}(\text{tetren})\}_6](\text{ClO}_4)_9$,^{10,13} which we label as CrCu_6 , CrNi_6 , and CrMn_6 , respectively. In these molecules a Cr(III) ion is surrounded by six cyanide ions, each bonded to a Cu(II), Ni(II), or Mn(II) ion. The coordination sphere of Cr and Cu/Ni/Mn can be described as slightly distorted octahedral. The objective in this work is to find the spin-spin correlation time $\tau(T)$ in the three systems, and to compare them. Our main findings are (i) τ is nearly T independent at low temperatures, and (ii) at very low temperature τ does not depend on S or J in this isotropic case.

In Fig. 1 we show the magnetization M per molecule in units of μ_B as a function of applied field H for the three molecules. The data are taken at $T = 2$ K. In all cases M increases as the applied field is increased. The magnetization reaches a saturation value of $\frac{9}{2}g\mu_B$, $\frac{15}{2}g\mu_B$, and $\frac{27}{2}g\mu_B$ in CrCu_6 , CrNi_6 , and CrMn_6 , respectively. These saturation

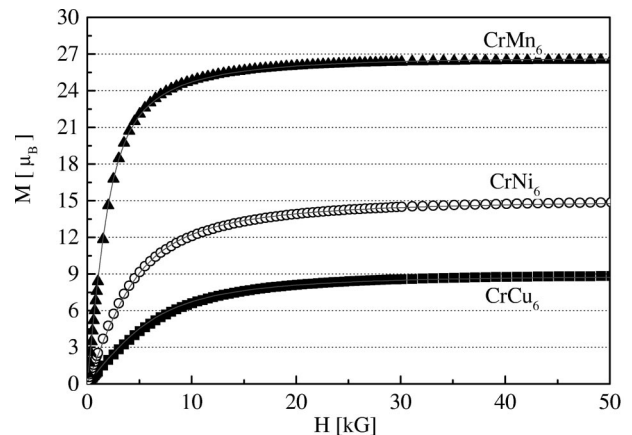


FIG. 1. The magnetization of CrCu_6 , CrNi_6 , and CrMn_6 as a function of the external applied field at $T = 2$ K, respectively. The solid lines are $S = 9/2$, $S = 15/2$, and $S = 27/2$ Brillouin functions (see text).

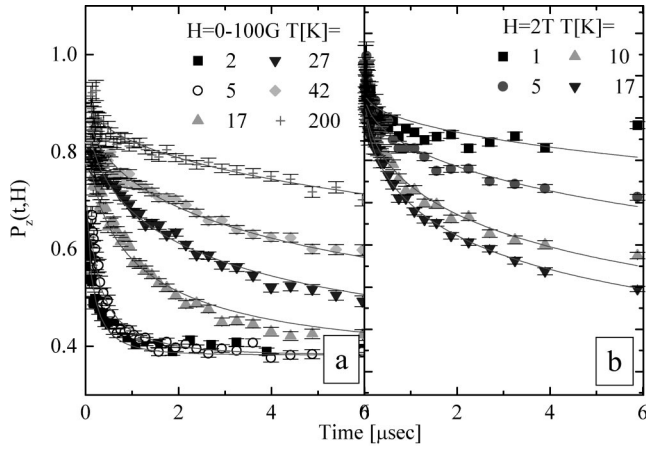


FIG. 2. Muon spin polarization as a function of time in CrNi₆. (a) At zero field and different temperatures. (b) At field $H=20$ kG and different temperatures. The solid lines are fits of the data to square-root exponential functions.

values are consistent with six Cu ($S=1/2$), Ni ($S=1$), or Mn ($S=5/2$) ions ferromagnetically (or antiferromagnetically in the case of CrMn₆) coupled only to a Cr ion of spin $3/2$. The solid lines are Brillouin functions of the respective S . In Refs. 10–13 the susceptibility was fitted to the one expected from the Heisenberg Hamiltonian and the values $J_{\text{CrCu}_6}=77$ K, $J_{\text{CrNi}_6}=24$ K, and $J_{\text{CrMn}_6}=-11$ K were found. Therefore, the highest-spin value of each molecule is well separated from other spin states (a few tens of degrees Kelvin). High-field electron-spin-resonance measurements (on CrNi₆) (Ref. 14) and susceptibility measurements (on CrCu₆, CrNi₆, and CrMn₆) found no evidence for anisotropy, namely, $D\approx 0$. This is consistent with the octahedral character of the molecules.

In our μSR experiments we measure the polarization $P(t, H)$ of a positive muon spin implanted in the sample, as a function of time t and magnetic field H , where $P(0, H)=1$. The field is applied in the direction of the initial muon polarization. The positive muon decays to a positron which is emitted in the direction of the muon spin, and the polarization as a function of time is reconstructed by the detection of the emitted positrons.

The measurements in all molecules are done at temperatures ranging from 25 mK up to 300 K, and in fields ranging between zero and 20 kG. These experiments were performed at both ISIS, U.K. and the Paul Scherrer Institute (PSI), Switzerland, exploiting the long time window in the first facility for slow relaxation (high T), and the high time resolution in the second facility for fast relaxation (low T).

In Figs. 2(a) and 2(b) we present the muon spin polarization as a function of time and for different temperatures in CrNi₆ in zero field, and in $H=20$ kG, respectively. In zero field, the relaxation rate increases, as the temperature is decreased, and saturates at ~ 5 K. The increase at high temperatures is caused by thermally activated transitions between excited spin states. However, at low temperatures, only the ground spin state is populated, and only transitions within the degenerate ground state are possible. In contrast, at $H=20$ kG, and temperatures lower than ~ 17 K, the relaxation

rate decreases as the temperature is decreased, and does not saturate.

In Ref. 15 we demonstrated that the magnetic field experienced by the muon in all molecules is dynamically fluctuating even at $T=50$ mK. We therefore analyze our data using spin-lattice relaxation theory. In this theory, the polarization of a local probe (muon or nucleus), in the fast fluctuation limit, is given by

$$P(H, t) = (P_0 - P_\infty) \exp[-t/T_1] + P_\infty, \quad (1)$$

where P_0 is the initial polarization, P_∞ is the equilibrium polarization,¹⁶

$$T_1(H) = A + BH^2, \quad (2a)$$

$$A = 1/\Delta^2 \tau, \quad (2b)$$

$$B = \gamma^2 \tau / \Delta^2, \quad (2c)$$

and γ is the probe gyromagnetic ratio. The correlation time τ and mean square of the transverse field distribution at the probe site in frequency units Δ^2 are defined by

$$\gamma^2 \langle \mathbf{B}_\perp(t) \mathbf{B}_\perp(0) \rangle = \Delta^2 \exp(-t/\tau). \quad (3)$$

The fast fluctuation limit is obeyed when $\tau \Delta \ll 1$.

In μSR , $P_\infty=0$, and the muon can occupy different sites in the sample, because the molecules are fairly large (~ 15 Å diameter) and present an organic surrounding around the metal ions. As a result one must average over Δ . Using the distribution¹⁶

$$\rho(\Delta) = \sqrt{\frac{1}{2\pi}} \frac{\Delta^*}{\Delta^2} \exp\left(-\frac{1}{8} \left[\frac{\Delta^*}{\Delta}\right]^2\right), \quad (4)$$

and allowing for a constant background (B_g) due to muons stopping outside the sample, one obtains

$$P(t) = P_0 \exp(-\sqrt{t/T_1^\mu}) + B_g, \quad (5)$$

where $1/T_1^\mu$ is the muon spin-relaxation rate. This form is in agreement with the experimental results (see below). In addition, Eq. (2a) still holds, while in Eqs. (2b) and (2c), Δ is replaced by Δ^* .

The solid lines in Fig. 2 are fits of the data to Eq. (5) where P_0 is a global parameter. The parameter B_g is free within 10% of its mean value since the high fields affect the positron trajectory in a manner that is reflected in B_g . The fit is satisfactory in all cases apart from the highest H and lowest T in CrNi₆. The relaxation rate $1/T_1^\mu$ in the different compounds, obtained from the fits, is presented in Fig. 3 as a function of temperature for different values of H . As pointed out above, at low fields $1/T_1^\mu$ increases with decreasing temperatures, and saturates at low temperatures. In addition the value of $1/T_1^\mu$ increases as the spin of the compound is higher, as expected from Eqs. (2) and (3), and the saturation temperature increases as the coupling constant J increases.

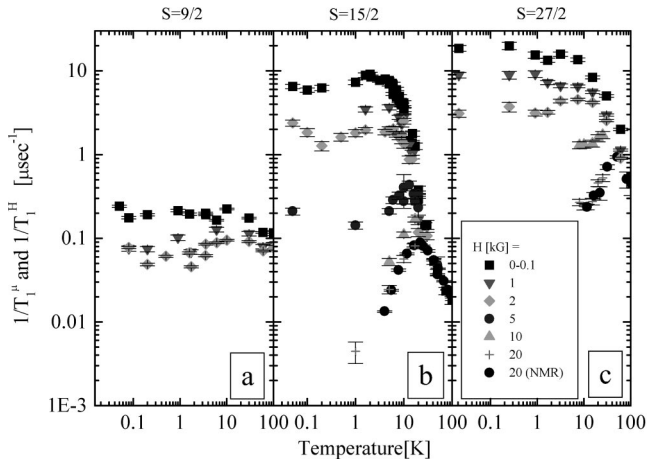


FIG. 3. $1/T_1$ as a function of temperatures for different external fields, measured by μ SR and NMR (after scaling) in (a) CrCu₆, (b) CrNi₆, and (c) CrMn₆.

This is in strong contrast to Mn₁₂ (Ref. 17) and Fe₈,¹⁸ where in zero field $1/T_1^\mu$ increases continuously upon cooling until the correlation time τ becomes so long that the molecule appears static in the muon dynamical window, and no T_1 saturation is observed at low temperatures.

In Fig. 4 we plot the average relaxation time $T_1^\mu(H)$ at $T \rightarrow 0$ as a function of H^2 for all compounds, for fields up to 2 kG (note the axis break). We find that T_1^μ obeys Eq. (2). This implies that the muon spin relaxation is indeed due to dynamical field fluctuations, and that at low T the field autocorrelation can be described by a single correlation time as long as the applied field is not too strong. At high fields (>2 kG) we find deviations (not shown) from the linear relation between T_1 and H^2 . The deviation might be due to the impact of the field on the spin dynamics, i.e., the correlation function given by Eq. (3). From the linear fits in Fig. 4, and taking $(\Delta^*)^2 = \gamma_\mu(AB)^{-1/2}$ from Eqs. (2b) and (2c), where $\gamma_\mu = 85.162$ MHz/kG, we find that for CrCu₆ $\Delta_0^* = 4.9 \pm 0.9$ MHz (57 ± 10 G), for CrNi₆ $\Delta_0^* = 26 \pm 2$ MHz (305 ± 25 G), and for CrMn₆ $\Delta_0^* = 38 \pm 2$ MHz

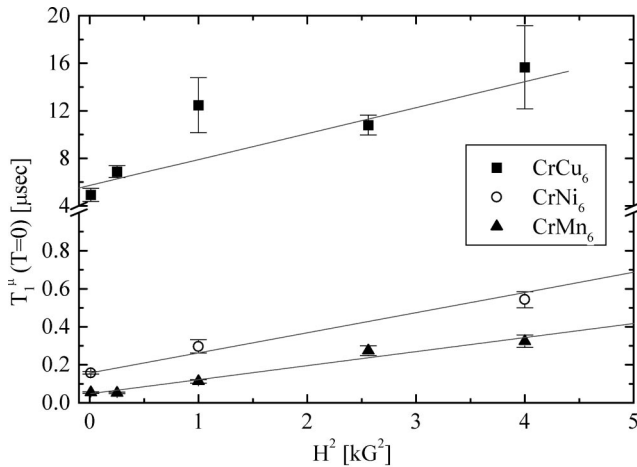


FIG. 4. The saturation relaxation time as a function of H^2 for CrCu₆, CrNi₆, and CrMn₆. The solid lines are linear fits of the data.

(446 ± 24 G); the subscript 0 stands for $T \rightarrow 0$. Using $\tau = (B/A\gamma_\mu^2)^{1/2}$ from the same equation we find $\tau_0 = 7 \pm 1$ ns for CrCu₆, $\tau_0 = 10 \pm 1$ ns for CrNi₆, and $\tau_0 = 11 \pm 1$ ns for CrMn₆. These values of Δ_0^* and τ_0 are self-consistent with the fast fluctuation limit. Most striking is the fact that all τ_0 values are quite close.

Although our data support a picture where the muon spin relaxes due to dynamically fluctuating magnetic fields, they leave open the interpretation of these fluctuations. Are they due to the fluctuations of the molecular spins or are they a result of muon diffusion, muonium formation, etc.? In order to address this question we performed proton NMR T_1 measurements. We find that in all applied fields smaller than 20 kG the proton T_1 is shorter than the experimental window around the peak in $1/T_1^\mu$. Only in a field of ~ 20 kG were we able to perform the experiment at all temperatures. We measure T_1 using a saturation $-t - \pi/2 - \pi$ pulse sequence. The proton polarization recovery follows Eq. (1) with $P_0 = 0$ from which we obtained T_1^H .

Since the proton gyromagnetic ratio $\gamma_H = 42.57$ MHz/kG is very different from that of the muon, we scale the NMR results and plot them together with the μ SR results in Fig. 3, for CrNi₆ [Fig. 3(b)] and CrMn₆ [Fig. 3(c)]. The scaling factor C used in Fig. 3 is 0.6 for CrNi₆ and 8.8 for CrMn₆. They were chosen so that the scaled NMR relaxation rates will agree with the μ SR rates at high T . After this scaling, we find good agreement between the μ SR and NMR data at all temperatures. In fields lower than 20 kG, where the NMR T_1 was measurable only at high T , we obtained the same agreement between the two techniques.

The scaling factor provides information on the ratio of the field experienced by a muon and a proton. At high temperatures where T_1 shows no field dependence one can assume that $A \gg BH^2$ in Eq. (2), and therefore $1/T_1 = \Delta^2 \tau$. Using the definition of Δ^2 given in Eq. (3) we can write $C \equiv (\gamma_H/\gamma_\mu)^2 \langle T_1^H/T_1^\mu \rangle = \langle \mathbf{B}_\perp^2 \rangle^\mu / \langle \mathbf{B}_\perp^2 \rangle^H$ where $\langle \mathbf{B}_\perp^2 \rangle^H$ is the rms of the transverse field at the proton site, and $\langle \mathbf{B}_\perp^2 \rangle^\mu$ is the rms of the field at the muon site in its general sense given by Eq. (4). The proximity of C to 1 especially in the CrNi₆ is very encouraging and suggests that the muons experience similar fields as the protons in this system. Thus, we prove that in both techniques we are measuring the probe's spin-lattice relaxation time due to the molecular spin fluctuations.

Finally, we would like to obtain the correlation time at all temperatures. This could be calculated from T_1^μ combined with magnetization measurements, at zero (or very low) fields. In zero-order approximation we assume that $\langle \mathbf{B}_\perp^2 \rangle$ is proportional to $\langle \mathbf{S}^2 \rangle$ which is different from $S(S+1)$ since at temperatures $k_B T \sim J$, states other than the ground state S can be populated. Therefore in zero field

$$\frac{1}{T_1}(T) = \frac{\Delta_0^{*2} \langle S^2 \rangle(T) \tau(T)}{S(S+1)}. \quad (6)$$

Taking

$$\langle S^2 \rangle(T) = \frac{3k_B T \chi(T)}{N(g\mu_B)^2}, \quad (7)$$

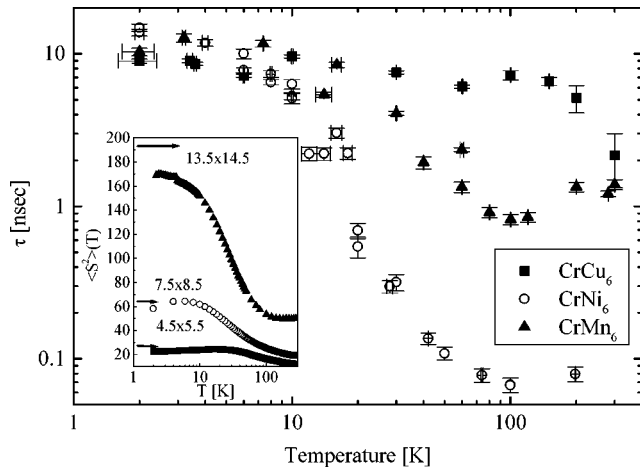


FIG. 5. The correlation time τ as given by Eq. (8) as a function of temperature for CrCu_6 , CrNi_6 , and CrMn_6 . The inset shows $\langle S^2 \rangle(T)$ as obtained from Eq. (7).

where N is the number of molecules, μ_B is the Bohr magneton, k_B is the Boltzmann factor, and $g=2$, we find

$$\tau(T) = \frac{(g\mu_B)^2}{3k_B} \frac{S(S+1)}{T_1(T)T\chi(T)\Delta_0^{*2}}. \quad (8)$$

In the insets of Fig. 5 we present $\langle S^2 \rangle(T)$, obtained from $H \rightarrow 0$ dc-susceptibility measurements and Eq. (7), as a function of temperature for CrCu_6 , CrNi_6 , and CrMn_6 . In Fig. 5 we present $\tau(T)$ as calculated using Eq. (8) for the different compounds. The T dependence of the correlation time $\tau(T)$, unlike the muon spin-lattice relaxation rate, reflects the dynamics of the molecular spin without the T dependence of the field at the muon site. At $T \sim 100$ K there is more than one order of magnitude difference in τ between the different molecules. As the temperature is lowered the correlation time in all compounds increases as the temperature is decreased, but reaches a *common saturation value* of ~ 10 ns (within

experimental error) at $T \sim 10$ K. At this temperature only the ground state S is populated. In other words, when the HSM's are formed they all have the same correlation time at low T .

At very low temperatures one can interpret the correlation time τ in terms of a broadening of the spin levels, due to interactions between a molecular spin and other molecular spin, or the environment. This interaction is considered a perturbation, the strength of which should be of the order of $\hbar\tau^{-1}$. Therefore, our results give two major indications. First, the broadening in the $T \rightarrow 0$ limit is not due to phonons since these die out exponentially with temperature at 0.05–1 K. Second, the broadening cannot be explained by interactions which are quadratic in S or have higher S dependence. This rules out the dipolar interaction between neighboring molecules since in the three compounds the nearest-neighbor distance is ~ 15 Å. Similarly, crystal-field terms which are allowed by the octahedral symmetry (S^4 or higher¹⁹) are unlikely.

The only mechanism suggested to date for level broadening of anisotropic HSM's, which is weakly (linear) S dependent, is the hyperfine interaction between nuclear and electronic spins. This mechanism can account for the finite spin-lattice relaxation rate at very low temperatures.²⁰ The hyperfine interactions in anisotropic high-spin molecules were studied recently,^{22,23} and their effect on QTM is becoming clearer.^{24,25} We believe that this interaction also governs the fluctuations of the isotropic molecules at very low temperatures ($T < 3$ K). However, at high temperature ($T > 10$ K) the fluctuations are governed by spin-phonon interactions.²¹

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