Quantum fluctuations of the magnetization in high spin molecules – a \(\mu\)SR study

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Abstract

Using zero field (ZF) and longitudinal field (LF) \(\mu\)SR we study the magnetic properties of high spin molecules (HSM) with spin \(S = \frac{32}{2}\) and \(\frac{27}{2}\). The LF-\(\mu\)SR at very low temperatures suggests that in both our samples dynamical field fluctuations are responsible for the muon relaxation. The relaxation rate \(\lambda\) increases as the temperature decreases and then saturates below \(T < T_B\) indicating that the dynamics is of quantum nature. The fluctuation rate at \(T \to 0\) of the different samples is compared. © 2000 Elsevier Science B.V. All rights reserved.

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High spin molecules (HSM) consist of magnetic ions coupled by ferromagnetic or antiferromagnetic interactions. These molecules crystallize in a lattice where neighboring molecules are magnetically separated, yielding, at low temperatures, noninteracting giant spins \(S\). Due to magneto-crystalline anisotropy, the dominant part of the Hamiltonian is an even function of \(S\) \cite{[1,2]}, and when the temperature is much lower than some anisotropy barrier, the only possible relaxation mechanism is of quantum mechanical origins.

In this paper we report experiments on two compounds \([\text{Cr(CN)}\text{Ni(tetren)}_6]\text{ClO}_4\)\(_9\) and \([\text{Cr(CN)}\text{Mn(trispicmeen)}_6]\text{ClO}_4\)\(_9\) denoted here as \(\text{CrNi}_6\) and \(\text{CrMn}_6\), respectively. The \(\text{CrNi}_6\) magnetic cores are situated on an ordered lattice, where the distance between the two neighboring cores is 15.68 Å, while the distance between a Cr ion and a Ni ion in the same core is 5.28 Å. The \(\text{CrMn}_6\) structure is not fully known but seems to be amorphous. The Hamiltonian of these systems at temperatures high above the anisotropy energy was found to agree with the form \(H = \sum_M J_{\text{Cr}-M} S_{\text{Cr}} S_M\) (where \(M\) is either Ni or Mn). In \(\text{CrNi}_6\) \cite{[2]}, the \(\text{Cr}^{3+}\) ion \((S = \frac{3}{2})\) interacts ferromagnetically with 6 Ni\(^{2+}\) ions \((S = 1)\) and creates a ground state of total spin \(S = \frac{15}{2}\) \cite{[3,4]}. Susceptibility measurements show that \(J_{\text{Cr}-\text{Ni}} = -24\) K, and the blocking temperature is \(T_B = 4.1\) K \cite{[2]}. In \(\text{CrMn}_6\) the interaction between the \(\text{Cr}^{3+}\) ion \((S = \frac{3}{2})\) and 6 Mn\(^{2+}\) ions \((S = \frac{5}{2})\) is antiferromagnetic \cite{[5,6]}, and the total spin of the ground state is \(S = \frac{27}{2}\). Similar susceptibility measurements \cite{[5,6]} show \(J_{\text{Cr}-\text{Mn}}\)
Fig. 1. (a) The variation of the asymmetry in CrNi$_6$ as the temperature is changed. (b) The variation of the asymmetry in CrNi$_6$ as the field is changed.

Fig. 2. The relaxation rate of the asymmetry as a function of temperature for different magnetic fields. The relaxation rate saturates at low temperatures.

The asymmetry in CrNi$_6$ is presented in Fig. 1(a). As the temperature is decreased towards 6 K, the relaxation rate increases. However, below 6 K there is no change in $A(t)$ indicating that the relaxation rate reaches saturation at $T_{c}^{\text{CrNi}}$. Such a saturation of the relaxation rate suggests that the fluctuations below $T_{c}^{\text{CrNi}}$ is of quantum nature. Again the same temperature dependence was observed in CrMn$_6$, but with a saturation of the relaxation at 10 K $\equiv T_{c}^{\text{CrMn}}$.

We fit the asymmetry in ZF or LF using the form $A(t) \propto e^{-t/\lambda}$, where $\beta$ varies between samples but is a global parameter for a specific sample. In CrNi$_6$ and CrMn$_6$ we find the best $\beta$ to be 0.5 and 0.3, respectively. In Fig. 2 the relaxation rate for both CrNi$_6$ and CrMn$_6$ is plotted as a function of temperature for different LF values. One can see that as the temperature is decreased the relaxation rate is increased, and reaches saturation at a $T_c$ which is different for different compounds. At high temperatures the relaxation is field independent, and becomes field dependent at lower temperatures.

The solid lines in Fig. 2 are fits of the relaxation rate $\lambda$ to a function of the form

$$\lambda(T, H) = \frac{1}{Q(H_L) + C \exp(-U/T)},$$

where $C$ and $U$ are global parameters for all fields, $C = 86 \pm 12$, $1.5 \pm 0.4 \mu$s and $U = 63 \pm 2$, $73 \pm 7$ K for CrNi$_6$ and CrMn$_6$, respectively. This
shows that the inverse relaxation rate (relaxation time) has a field-dependent part which is temperature independent \( Q(H_L) \), and a temperature-dependent part which is field independent \( C \exp(-U/T) \). The value of \( Q(H_L) \) is the value of the relaxation time at low temperatures (saturation value). This parameter is found to be proportional to the LF squared, \( H_L^2 \), as shown in Fig. 3.

The stretched exponential relaxation combined with the fact that \( \lambda^{-1} \) depends linearly on \( H_L^2 \) could be explained by a single field–field correlation function \([5]_n \) \( \langle B^*_L(0)B_L(t) \rangle = \langle B^*_L \rangle e^{-\nu t} \) where \( \nu \) is the field–field correlation rate, and \( \langle B^*_L \rangle \) is the mean squared field (at a given muon site), combined with multiple muon occupation sites. The multiple sites introduce a distribution of \( \langle B^*_L \rangle \). For long times \( vt \gg 1 \) (which is satisfied in our case) the relaxation rate \( \lambda^{-1} \) reduces to \([8,9]_n \)

\[
\frac{1}{\lambda} = \frac{1}{2va^2}H_L^2 + \frac{\nu}{2\gamma a^2}, \tag{2}
\]

where \( a \) represents the range of possible \( \langle B^*_L \rangle \). From Fig. 3 and Eq. (2), we find \( a_{\text{Ni}} = 214 \pm 4 \) G and \( a_{\text{Mn}} = 389 \pm 21 \) G for \( \text{CrNi}_6 \) and \( \text{CrMn}_6 \), respectively. The values of \( a \) in the two samples cannot be directly compared since we have used different \( \beta \) values. However, it is encouraging that the ratio \( a_{\text{Ni}}/a_{\text{Mn}} \) differs from the ratio of the expectation values of \( \sqrt{S^2} \), which is \( \sqrt{\frac{15}{2} (\frac{5}{2} + 1)/\frac{12}{2} (\frac{7}{2} + 1)} \), in the two compounds by 4% only. This suggests that the muons occupy roughly the same sites in the two samples.

In addition, we calculated the fluctuations rates \( \tau^{-1} = \nu/2 = 50 \pm 5 \) MHz and \( 60 \pm 15 \) MHz for \( \text{CrNi}_6 \) and \( \text{CrMn}_6 \), respectively. Quantum tunneling theories predict a strong dependence of the tunneling rate on the spin value, \( \tau^{-1} = DS^2/\pi Sh(H_L/S^2)^{28 \,[1,2,10–12]} \) \( H_L \) is the transverse part of the Hamiltonian which induces tunneling and \( T_B \sim DS^2 \). However, according to this calculation the fluctuation rate yields \( H_L \approx 4.3 \) and 5.7 kG in \( \text{CrNi}_6 \) and \( \text{CrMn}_6 \), respectively. These fields are not consistent with the root mean squared field experienced by the muon. We thus conclude that the description of the quantum dynamics in this system could not be mapped into the double potential picture which is useful in other HSM such as \( \text{Mn}_{12} \) \([13]_n \) and \( \text{Fe}_8 \) \([14]_n \). However, the ratio \( J_{\text{Cr}–\text{Ni}}S_{\text{Cr}–\text{Ni}}/J_{\text{Cr}–\text{Mn}}S_{\text{Cr}–\text{Mn}} \) of the fluctuation rates in both samples \( v_{\text{Ni}}/v_{\text{Mn}} \) is equal to the coupling energy between the ions.

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References

