ELSEVIER

Physica B 289–290 (2000) 106–109

PHYSICA B

www.elsevier.com/locate/physb

Quantum fluctuations of the magnetization in high spin molecules – a μSR study

Zaher Salman[a,*], Amit Keren[a], Philippe Mendels[b], Ariane Scuiller[c], Michel Verdaguer[c]

[a]*Physics Department, Technion-Israel Institute of Technology, Haifa 32000, Israel*
[b]*Laboratoire de Physique des Solides, Université Paris Sud, 91405 Orsay, France*
[c]*Laboratoire de Chimie Inorganique et Matériaux Moléculaires, Université Pierre et Marie Curie, 75252 Paris Cedex 05, France*

Abstract

Using zero field (ZF) and longitudinal field (LF) μSR we study the magnetic properties of high spin molecules (HSM) with spin $S = \frac{15}{2}$ and $\frac{27}{2}$. The LF-μSR at very low temperatures suggests that in both our samples dynamical field fluctuations are responsible for the muon relaxation. The relaxation rate λ increases as the temperature decreases and then saturates below $T < T_c$ indicating that the dynamics is of quantum nature. The fluctuation rate at $T \to 0$ of the different samples is compared.

Keywords: High spin molecules; Quantum fluctuations; Tunneling; Dynamic

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 $\boldsymbol{S}$. Due to magneto-crystalline anisotropy, the dominant part of the Hamiltonian is an even function of $\boldsymbol{S}$ [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 $[Cr(CN)Ni(tetren)_6](ClO_4)_9$ and $[Cr(CN)Mn(trispicmeen)_6](ClO_4)_9$ denoted here as $CrNi_6$ and $CrMn_6$, respectively. The $CrNi_6$ 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 $CrMn_6$ 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 $H = \sum_M J_{Cr-M} S_{Cr} S_M$ (where M is either Ni or Mn). In $CrNi_6$ [2], the Cr^{3+} ion ($S = \frac{3}{2}$) interacts ferromagnetically with 6 Ni^{2+} ions ($S = 1$) and creates a ground state of total spin $S = \frac{15}{2}$ [3,4]. Susceptibility measurements show that $J_{Cr-Ni} = -24$ K, and the blocking temperature is $T_B = 4.1$ K [2]. In $CrMn_6$ the interaction between the Cr^{3+} ion ($S = \frac{3}{2}$) and 6 Mn^{2+} ions ($S = \frac{5}{2}$) is antiferromagnetic [5,6], and the total spin of the ground state is $S = \frac{27}{2}$. Similar susceptibility measurements [5,6] show J_{Cr-Mn}

* Corresponding author. Tel.: +972-4-8292044; fax: +972-4-8221514.
E-mail address: zaher@physics.technion.ac.il (Z. Salman).

0921-4526/00/$ - see front matter
PII: S0921-4526(00)00271-4

$= 11.5$ K and a blocking temperature of $T_B = 5.3$ K. The different spin values of the samples allow us to investigate the effect of S on the fluctuation rate which we have determined by μSR.

Our experiments at high temperatures (weak relaxation) were performed at ISIS, and at low temperature (strong relaxation) at PSI. In Fig. 1(b) we present the LF dependence of the asymmetry $A(t)$ in $CrNi_6$ at base temperature (50 mK). As can be seen the relaxation rate decreases as the field is increased. Two aspects of the data indicate that the muon polarization relaxes due to dynamical field fluctuations; the first is that no recovery ($\lim_{t\to\infty} A(t) \equiv A_\infty = 0$) is observed. Such recovery ($A_\infty = A(0)/3$) appears in cases where the muon experiences a static local field and zero external field [7]. The second is that the time scale of relaxation $[1/\lambda]$ in ZF is 1 μs; if this field were static it would have been of the order of $[B] \approx 10$ G (using $[B] = [\lambda]/\gamma_\mu$ where γ_μ is the muon gyromagnetic ratio). Such a field should have been completely decoupled ($\lim_{t\to\infty} A(t) = A(0)$) with ~ 100 G LF or more [7]. However, even fields as high as 5000 G do not decouple the relaxation. Therefore, we conclude that even at 50 mK the $CrNi_6$ spins are dynamically fluctuating. Similar experiments and line of arguments indicate that $CrMn_6$ spins are also dynamically fluctuating at base temperature.

The temperature dependence of the asymmetry in $CrNi_6$ is presented in Fig. 1(a). As the temperature is decreased towards 6 K $\equiv T_c^{CrNi}$ 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^{CrNi}. Such a saturation of the relaxation rate suggests that the fluctuations below T_c^{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 $\equiv T_c^{CrMn}$.

We fit the asymmetry in ZF or LF using the form $A(t) \propto e^{-(\lambda t)^\beta}$, where β varies between samples but is a global parameter for a specific sample. In $CrNi_6$ and $CrMn_6$ we find the best β 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

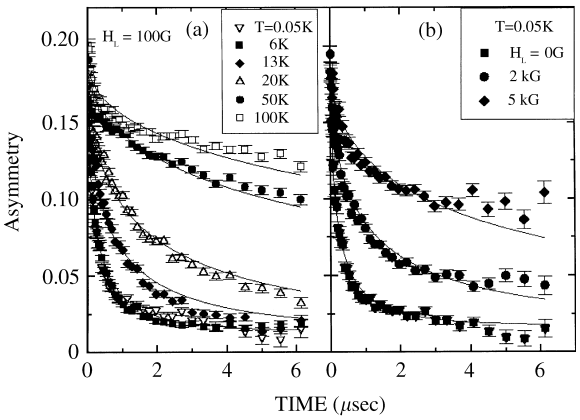

Fig. 1. (a) The variation of the asymmetry in $CrNi_6$ as the temperature is changed. (b) The variation of the asymmetry in $CrNi_6$ as the field is changed.

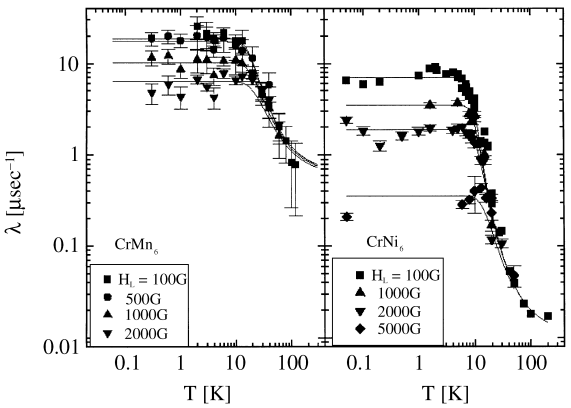

Fig. 2. The relaxation rate of the asymmetry as a function of temperature for different magnetic fields. The relaxation rate saturates at low temperatures.

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 λ to a function of the form

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

where C and U are global parameters for all fields, $C = 86 \pm 12$, 1.5 ± 0.4 μs and $U = 63 \pm 2$, 73 ± 7 K for $CrNi_6$ and $CrMn_6$, respectively. This

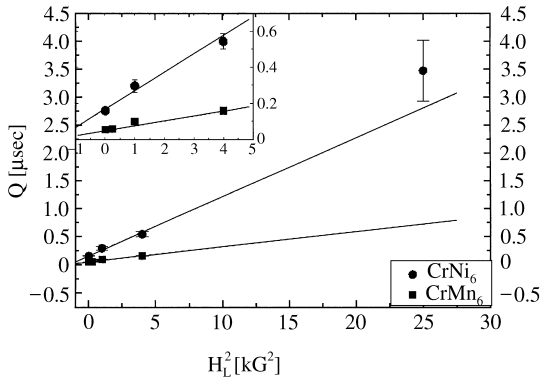

Fig. 3. The saturated relaxation time Q as a function of H_L^2 for both $CrMn_6$ and $CrNi_6$. The solid lines are linear fits of Q versus H_L^2. The inset shows the low fields range.

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

$$\frac{1}{\lambda} = \frac{1}{2\nu a^2}H_L^2 + \frac{\nu}{2\gamma_\mu^2 a^2}, \tag{2}$$

where a represents the range of possible $\langle B_\perp^2\rangle$. From Fig. 3 and Eq. (2), we find $a_{Ni} = 214 \pm 4$ G and $a_{Mn} = 389 \pm 21$ G for $CrNi_6$ and $CrMn_6$, respectively. The values of a in the two samples cannot be directly compared since we have used different β values. However, it is encouraging that the ratio a_{Ni}/a_{Mn} differs from the ratio of the expectation values of $\sqrt{S^2}$, which is $\sqrt{\frac{15}{2}(\frac{15}{2}+1)/\frac{27}{2}(\frac{27}{2}+1)}$, 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 ± 15 MHz for $CrNi_6$ and $CrMn_6$, respectively. Quantum tunneling theories predict a strong dependence of the tunneling rate on the spin value, $\tau^{-1} = DS^2/\pi S\hbar(H_\perp S/DS^2)^{2S}$ [1,2,10–12] ($H_\perp$ 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 $H_\perp \approx 4.3$ and 5.7 kG in $CrNi_6$ and $CrMn_6$, 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 Mn_{12} [13] and Fe_8 [14]. However, the ratio $J_{Cr-Ni}S_{Cr}S_{Ni}/J_{Cr-Mn}S_{Cr}S_{Mn}$ of the fluctuation rates in both samples ν_{Ni}/ν_{Mn} is equal to the coupling energy between the ions.

These experiments were supported by the European Union through its TMR Program for Large-Scale Facilities, the French Israeli cooperation program AFIRST and the Israeli Ministry of Science.

References

[1] J. van Hemmen, A. Sütö, Europhys. Lett. 1 (1986) 481.
[2] J. van Hammen, A. Sütö, in: L. Gunther, B. Barbara (Eds.), Quantum Tunneling of the Magnetization – QTM '94, Kluwer Publishing, Dordrecht, 1995, p. 189.
[3] T. Mallah, S. Ferlay, A. Scuillier, M. Verdaguer, Molecular Magnetism: A Supramolecular Function, NATO ASI Series, Vol. C474, Reidel, Dordrecht, 1996.
[4] T. Mallah et al., J. Chem Soc. Chem. Commun. 1 (1995) 61.
[5] A. Scuiller, T. Mallah, A. Nivorozkhin, M. Verdaguer, P. Veillet, New J. Chem. 20 (1996) 1.
[6] A. Scuiller, T. Mallah, M. Verdaguer, A. Nivoroskhin, J. Tholence, P. Veillet, New J. Chem. 20 (1996) 1.
[7] P. Dalmas de Réotier, A. Yaouanc, J. Phys.: Condens. Matter 9 (1997) 9113–9166.
[8] Y. Uemura, T. Yamazaki, D.R. Harshman, M. Senba, E.J. Ansaldo, Phys. Rev. B 31 (1985) 546.
[9] A. Keren, Phys. Rev. B 50 (1994) 10 039.
[10] D. Garanin, J. Phys. A 24 (1991) L61.
[11] D. Garanin, X. Martínez Hidalgo, E. Chudnovsky, Phys. Rev. B 57 (1998) 13 639.

[12] E. Chudnovsky, J. Tejada, in: D. Edwards (Ed.), Macroscopic Quantum Tunneling of the Magnetic Moment, Cambridge University Press, Cambridge, MA, 1998 (Chapter 7).

[13] J. Friedman, M. Sarachik, J. Tejada, R. Ziolo, Phys. Rev. Lett. 76 (1996) 3830.

[14] C. Sangregorio, T. Ohm, C. Paulsen, R. Sessoli, D. Gatteschi, Phys. Rev. Lett. 78 (1997) 4645.