Transverse magnetic field effects on the relaxation time of the magnetization in Mn12 measured by ^{55}Mn-NMR

Y. Furukawa [a,1], K. Watanabe [a], K. Kumagai [a] F. Borsa [b] D. Gatteschi [c]

[a] *Division of Physics, Graduate school of Science, Hokkaido University, Sapporo 060-0180, Japan*
[b] *Department of Physics and Astronomy, Ames Laboratory, Iowa State University, Ames, Iowa 50011, USA and Dipartimento di Fisica "A Volta" e Unita'INFM di Pavia, Via Bassi 6, 271000 Pavia, Italy*
[c] *Department of Chemistry, University of Florence, Via Maragliano 77, 50144 Firenze, Italy*

Abstract

The longitudinal (H_Z) and transverse (H_T) magnetic field dependence of the relaxation time of the magnetization in Mn12 in its S=10 ground state was measured by NMR. The minima in the relaxation time at the field for level crossing are due to the quantum tunneling of the magnetization. The shortening of the relaxation time under the application of H_T is shown to be due mainly to the reduction of the energy barrier.

Key words: Mn12; quantum tunneling of the magnetization ; NMR

Mn12-acetate, $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$ (in short Mn12) has attracted much interest after the discovery of the quantum tunneling of the magnetization (QTM) [1]. The Mn12 contains four Mn^{4+} (s=3/2) ions in a central tetrahedron surrounded by eight Mn^{3+} (s=2) ions with two nonequivalent sites [2]. Strong antiferromagnetic interactions between Mn^{4+} and Mn^{3+} give rise to a ferrimagnetic state of high spin S=10 ground state [3]. Such a ferrimagnetic internal magnetic structure of the Mn12 was directly confirmed from the microscopic point of view by ^{55}Mn-NMR [4].

The S=10 ground state of the cluster can be described by a simple spin Hamiltonian

$$H = -DS_z^2 - BS_z^4 + g\mu_B \mathbf{HS} \qquad (1)$$

where D∼0.55 (K) and B∼1.2 (mK) are anisotropy parameters [5]. The anisotropy introduces a large energy barrier for the reorientation of the S=10 spins, giving rise to a superparamagnetic behavior at low temperature [6]. The last term in eq.(1) describes the Zeeman interaction whereby the direction of the external magnetic field with respect to the easy-axis (c-axis) is important in QTM phenomena. The longitudinal field (H_Z) parallel to the easy-axis shifts the initially pairwise degenerate magnetic ±m substates and for certain values of the field, i.e, 0.45n (n:integer) induces level crossings and consequent QTM. On the other hand, the transverse field (H_T) perpendicular to the easy-axis is considered to enhance QTM because of the increase of the tunneling splitting originated from a term of $g\mu_B S_x H_x$ in eq. (1). Furthermore, the H_T loweres the barrier according to the relation $U_0(1\text{-}H_T/H_A)^2$ where U_0 is the barrier at zero magnetic field and H_A is the field at which the barrier disappears.

In this paper, we report the effects of the transverse magnetic field on the relaxation time τ of the magnetization of Mn12 in its S=10 ground state measured by ^{55}Mn-NMR. It has been already reported in Mn12 that the τ can be measured by monitoring the change of the intensity of ^{1}H-NMR signals in time after the inversion of the magnetic field [7]. Using the same field inversion method, the τ was measured at T=1.94 K also by ^{55}Mn-NMR [8]. Here we have measured τ by ^{55}Mn-NMR signals at 2.4 K using the field inversion method described in ref. 7. The observed relaxation behavior measured at 2.4 K is well fitted by a single exponen-

[1] Corresponding author. E-mail: furu@phys.sci.hokudai.ac.jp

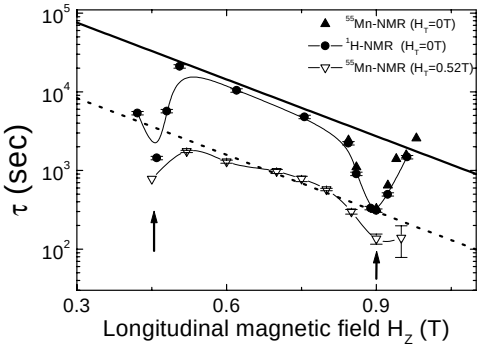

Fig. 1. H_z-dependence of τ(H) for both H_T=0 and 0.52T measured at T=2.4 K by NMR. Thin lines are just for eye-guide. For details, see text.

tial function as exp(-t/τ), in contrast to a square-root t behavior at T=1.96 K reported previously [8]. The details for the experimental procedure were described in ref. 7. The oriented sample used here is the same one used in our previous papers [4,7].

Figure 1 shows the longitudinal field dependence of relaxation time of the magnetization (τ(H)) measured at 2.4 K by ^{55}Mn-NMR (closed triangles). Previous data [7] obtained by ^{1}H-NMR are also plotted in Fig. 1. The good agreement with the new data obtained by ^{55}Mn-NMR indicates that our NMR method is robust and independent from the nucleus used as a probe. As can be seen in the figure, τ(H) shows minima at H_Z=0.45 and 0.9 T, as indicated by arrows in the figure. The field values agree with the critical fields where the magnetic level crossing occurs. Thus the minima are considered to be a signature of the QTM.

Except for the minima due to QTM, the H_Z-dependence of τ(H) follows a thermal activated law of τ(H)=$\tau_0$exp((U_0-13.3H_Z)/k_BT) with $\tau_0=3\times10^{-7}$ (sec), T=2.4 K and an energy barrier $U_0=D_{\rm eff}S^2$=67K ($D_{\rm eff}=D+BS^2$) at the zero magnetic field as shown by a thick solid line in the figure. This is consistent with background thermal excitations over the barrier as modified by the applied longitudinal magnetic field.

In order to investigate the effects of the transverse magnetic field for the relaxation time of magnetization, we have measured the H_Z-dependence of the relaxation time τ(H) while applying a constant transverse magnetic field of H_T=0.52T. The results are shown by open triangles in the figure. As can be seen, all τ(H) under application of the transverse field H_T=0.52T is shorter than the data measured in H_T=0 at the same H_Z. We can see the dips of τ(H) at H_Z=0.45 and 0.9 T.

The H_Z-dependence of τ(H) for the background thermal excitation over the energy barrier can be fitted by the equation of τ(H)=$\tau_0$exp((61 -13.3H_Z)/k_BT) as shown by the broken line in the figure. This result indicate that the height of the energy barrier reduces from 67 K at H_T=0 to 61 K at H_T=0.52T. The value of 61 K is very close to the value 60.2 K estimated from the relation of 67(1-H_T/H_A)^2 with H_A =2$D_{\rm eff}$S$\sim$10T and H_T=0.52T. The good agreement between the calculated energy barrier and the experimental result is a direct confirmation of the reduction of the energy barrier due to the transverse magnetic field. Similar results were also reported by measuring the H_T dependence of the relaxation rates of the magnetization around $H_Z\sim$0.45T [9].

As for the effects of H_T on QTM, the critical fields at the dips in H_Z-dependence of τ(H) does not change when the H_T=0.52T is applied. This indicates that the critical fields for QTM are determined only by the longitudinal field component H_Z. On the other hand, as for the magnitude of the dips, we would have expected a bigger effect at the critical field for level crossing as a result of the bigger tunneling splitting in transverse field. Instead, we could not detect any appreciable change of the dips of τ(H) at the critical fields. This result suggests a negligible enhancement of QTM under application of a small transverse magnetic field. Further measurements with higher values of H_T are underway to clarify this point.

In conclusion, we have succeeded in measuring the relaxation time of the magnetization by NMR and we could reproduce the minima in the τ(H) at the fields for level crossings which are considered to be a signature of the QTM. The reduction of the energy barrier under application of a transverse magnetic field was confirmed by the direct measurements of τ(H) utilizing NMR.

The present work is supported in part by a Grant-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Science, Sports and Culture of Japan. Ames Laboratory is operated for U.S. Department of energy by Iowa State University under Contract No. W-7405-Eng-82. This work at Ames Laboratory was supported by the Director for Energy Research, Office of Basic Energy Sciences.

References

[1] L. Thomas, et al., Nature (London) **383** (1996) 145.

[2] T. Lis, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **36** (1980) 2042.

[3] R. Sessoli, et al., J. Am. Chem. Soc. **115** (1993) 1804.

[4] Y. Furukawa, et al., Phys. Rev. B**64** (2001) 104401.

[5] Y. Zhong, et al., J. Appl. Phys. **85** (1999) 5636.

[6] R. Sessoli, et al., Nature (London) **365** (1993) 141.

[7] Y. Furukawa, et al., Phys. Rev. B**62** (2000) 14246.

[8] T. Kubo, et al., Physica B **294-295** (2001) 310.

[9] J. R. Friedman, et al., J. Appl. Phys. **81** (1997) 3978.