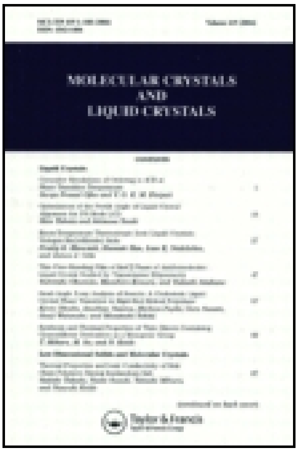

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55 Mn-NMR Study of Internal Magnetic Structure of the Molecular Nanomagnet Mn 12 -Acetate

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^{55}Mn-NMR Study of Internal Magnetic Structure of the Molecular Nanomagnet Mn$_{12}$-Acetate

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^{55}Mn nuclear magnetic resonance (NMR) measurements have been carried out in Mn12 clusters in order to investigate microscopically the magnetic properties of inner spin structure of the molecule in its high spin S=10 ground state. The external magnetic field dependence of ^{55}Mn-NMR spectrum gives a direct confirmation of the internal magnetic structure of the Mn12 cluster, in which spin moments of Mn^{4+} (S=3/2) ions are polarized antiparallel to that of Mn^{3+} (S=2) ions. It is proved that the microscopic spin configuration rotates rigidly when a field up to 8T is applied perpendicular to the easy-axis.

Keywords: Mn12 cluster; Internal structure; ^{55}Mn-NMR

INTRODUCTION

The nanoscale molecular magnets have recently attracted much interest after the discovery of quantum tunneling of the magnetization (QTM) and quantum coherent phenomena[1]. Among the magnetic clusters, [$Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4$] (in short Mn12) is one of the most investigated molecular magnet so far in which QTM has been observed[2]. The Mn12 cluster contains four Mn^{4+} (s=3/2) ions in a central tetrahedron surrounded by eight Mn^{3+} (s=2) ions with two nonequivalent sites[3], as shown in Figure 1. Strong antiferromagnetic interactions between Mn^{4+} and Mn^{3+} spins are considered to lead to a ferrimagnetic state of high spin S=10 ground state[4].

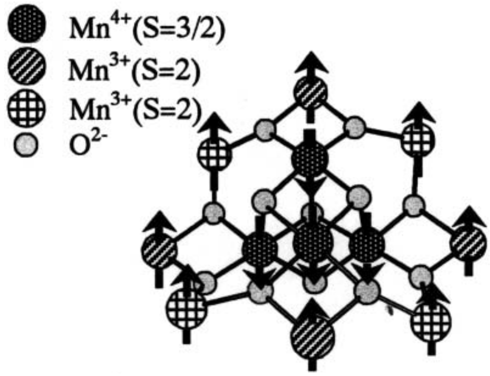

FIGURE 1 Structure of Mn12 cluster and orientation of the Mn moments in the ground state according to the standard picture.

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

$$H = DS^2 + BS^4 + g\mu_B \vec{S}\cdot\vec{H} \qquad (1)$$

where D ~ -0.6 (K) and B ~ -1.1 (mK) are anisotropy parameters[5]. The negative values for the parameters introduce a large energy barrier for the reorientation of the S=10 spins, giving rise to a superparamagnetic behavior at low temperature below ~ 3K[6]. The last term in eq.(1) describes the Zeeman interaction and the direction of the external magnetic field with respect to the easy-axis (*c*-axis) is important in QTM phenomena. The magnetic field parallel to the easy-axis removes the degenerate sublevels of the S=10 state, while transverse field perpendicular to the easy-axis does not modify the degeneracy but affects largely the tunnel splitting.

In this work, we have investigated microscopically the magnetic properties of internal spin structure of the Mn12 cluster by ^{55}Mn nuclear magnetic resonance (NMR) in the external magnetic field for directions both parallel and perpendicular to the easy-axis.

RESULTS AND DISCUSSIONS

Polycrystalline sample of $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]2CH_3COOH \cdot 4H_2O$ were prepared as described in Reference 4. The powdered material was mixed with Stycast 1266 and allowed to set in a magnetic field of 9T at 300K for several hours in order to obtain a sample with rigid orientation of the crystallites with their easy axis (*c*-axis). ^{55}Mn-NMR measurements were carried out utilizing a phase-coherent spin-echo pulse spectrometer.

In the superparamagnetic state of Mn12 cluster at T=1.5K, ^{55}Mn-NMR spectrum in the zero magnetic field consists of three distinct peaks with one sharp peak centered at 231MHz (P1) and two broad peaks centered at 277MHz (P2) and 365MHz (P3). The signals around 231MHz are assigned to Mn^{4+} (s=3/2) ions and the others are to Mn^{3+} (s=2) ions[7,8].

Figure 2 shows external magnetic field dependence of the resonance frequencies of the three signals in the spectrum where the magnetic field is applied along the easy-axis. With increasing external field, P1 shifts to higher frequency while the other two peaks (P2 and P3 of Mn^{3+} ions) shift to lower frequency. As the resonance frequency

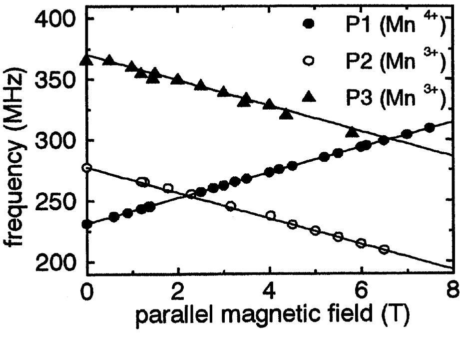

FIGURE 2 The magnetic field dependence of the resonance frequencies for each peak in the field parallel to easy-axis measured at T=1.5K.

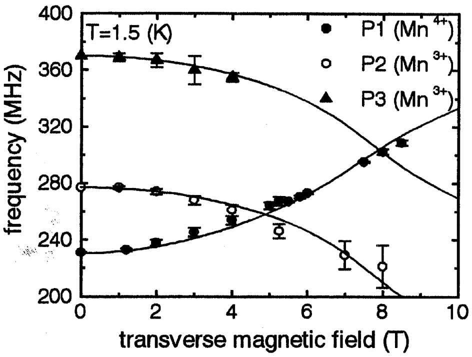

FIGURE 3 The dependence of the resonance frequencies for each peak on the field perpendicular to easy-axis measured at T=1.5K.

is proportional to the vector sum of internal field ($\mathbf{H}_{int}$) and external field ($\mathbf{H}_{ext}$) as $\omega_R = \gamma_N| \mathbf{H}_{int} + \mathbf{H}_{ext} |$, this result indicates that the direction of internal field at the Mn sites for Mn^{3+} ions is opposite to that for Mn^{4+} ions. Since the $\mathbf{H}_{int}$ is mainly originated from the core-polarization[7], $\mathbf{H}_{int}$ is negative and the direction of the internal fields at nuclear sites is opposite to that of the Mn spin moment. Thus we conclude that spin direction of Mn^{4+} ions is antiparallel to the external field, while that of Mn^{3+} ions is parallel to the external field, corresponding to the spin structure of magnetic core of Mn12 cluster shown in Figure 1.

In a case when the external magnetic field is applied perpendicular to the oriented axis (that is, the easy-axis), the dependence of the resonance frequencies for each peak on the field differs from the case for the parallel field, as shown in Figure 3.

As described above, the resonance frequency is proportional to the effective internal field at the nuclear site, which is a vector sum of both $\mathbf{H}_{int}$ due to spin moments and $\mathbf{H}_{ext}$ of external field i.e. $|\mathbf{H}_{eff}| = |\mathbf{H}_{int} + \mathbf{H}_{ext}|$. Thus the opposite field dependence of $|\mathbf{H}_{eff}|$ for Mn^{4+} and Mn^{3+} ions indicates that the direction of Mn^{4+} spin moments is antiparallel to that of Mn^{3+} spin moments. This leads to a conclusion that the individual spin moments of both Mn^{4+} and Mn^{3+} do not cant in the same direction of the transverse field but rotate rigidly maintaining the same relative spin configuration.

To analyze the experimental results more quantitatively, we have

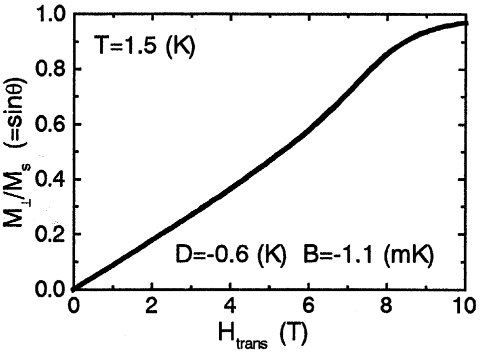

FIGURE 4 The calculated transverse magnetization ($M_\perp$) normalized by the saturated magnetization (Ms) at 1.5K with the parameters of D=-0.6 (K) and B=-1.1 (mK).

calculated the transverse field dependence of $|\mathbf{H}_{eff}|$ as follows. Under applying the transverse magnetic field, the direction of $\mathbf{H}_{int}$ does not coincide with the easy-axis because of canting of the magnetization (S=10) due to the field. The canting angle, θ between easy-axis and a direction of the magnetization under the field is expressed by $\theta = \sin^{-1}(M_\perp/Ms)$ where Ms is the saturated magnetization of S=10 ground state. The transverse field dependence of $\sin\theta$ can be obtained by calculating the transverse magnetization $M_\perp$ using the spin Hamiltonian of eq.(1). The calculated $M_\perp$/Ms is shown in Figure 4.

Using the calculated $\sin\theta = M_\perp/Ms$, the transverse field dependence of $|\mathbf{H}_{eff}|$ at Mn sites can be obtain from

$$\left|\overrightarrow{H_{eff}}\right| = \left|\overrightarrow{H_{int}} + \overrightarrow{H_{ext}}\right| = \sqrt{H_{int}^2 + H_{ext}^2 + 2H_{int}H_{ext}\sin\theta} \qquad (2)$$

where a sign of H_{int} is taken to be a negative for Mn^{3+} ions and a positive for Mn^{4+} ions, respectively. The solid lines in the Figure 3 show the calculated field dependence of resonance frequencies for each site, where the experimental results are well explained by the calculation. These results indicate that the ferrimagnetic spin state of the Mn12 cluster is not destroyed by the transverse magnetic field and the spin structure corresponding to the S=10 spin state is robust.

CONCLUSIONS

The internal magnetic structure of the Mn12 cluster was investigated microscopically by ^{55}Mn-NMR in its high spin S=10 ground state. We confirmed experimentally the inner magnetic structure of the cluster, as shown in Figure 1.The internal magnetic structure corresponding to the S=10 ground state has been shown to be stable even when the transverse magnetic field is applied. The transverse magnetization generated by the transverse field must result from a rigid rotation of the spin structure shown in Figure 1.

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