Nuclear magnetic relaxation of ^{1}H in molecular cluster magnet V_{15}

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Abstract

The temperature dependence of T_1 of ^{1}H in S=1/2 molecular magnet V_{15} was measured below 3.5T, including the critical field H_C=2.9T, where the ground state changes from |1/2, −1/2> to |3/2, −3/2>. The relaxation rate $1/T_1$ decreases remarkably with decreasing temperature. The results are interpreted in terms of the thermal fluctuation between two levels of S=1/2 induced by spin-phonon interaction. Around the level crossing fields of H=0 and 2.9T, $1/T_1$ becomes much less temperature dependent, which suggests the predominance of another relaxation mechanism associated with the level crossing.

Key words: V_{15}; ^{1}H NMR; nuclear-spin-lattice relaxaton

1. Introduction

Recently there has been a great interest in quantum tunneling of the magnetization in nano-scale molecular magnets. A molecular magnet V_{15} with a low spin of S=1/2 shows a step-wise magnetization curve which is associated with phonon-bath, though there is no energy barrier against the spin reversals [1][2]. This is contrary to the case of Mn_{12}AC and Fe_8 with the large spin of S=10 in which the tunneling is due to spin-bath. V_{15} is made of a lattice of molecules involving 15 V^{4+} (S=1/2) ions, which placed in a quasi-spherical layered structure formed of a triangle intervenueing between two hexagons. All the exchange interaction are anti-ferromagnetic. As a combined effect, the ground state of V_{15} is regarded to be constituted of three antiforromagnetically-coupled spins of S=1/2, as shown in Fig.1.(a). The magnitude of the effective anti-ferromagnetic exchange interactions J_0 between two of these resultant spins are a only 2.5K. The energy scheme of V_{15} at low temperatures is thus determined by configuration of S=1/2 and that of S=3/2, at $-3J_0/2$ above. When an applied field H_0 exceeds H_c=2.9T, the ground state changes from |1/2,−1/2> to |3/2,−3/2>.

Figure 1.(b) shows the energy scheme of V_{15} determined from the low-temperature magnetization measurement [1]. Thus V_{15} is viewed as a realization of a two-level system with a different configuratin of S=3/2 near the ground level.

In order to study the spin dynamics for V_{15}, we have measured the spin-lattice relaxation time T_1 of proton in V_{15} in the temperature range from 10K down to 0.5K in the field range of 0.3∼3.5T.

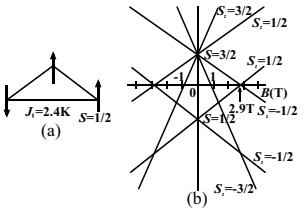

Fig. 1. (a)The resultant three spins of S=1/2 and effective anti-ferromagnetic exchange interactions J_0, (b)The energy scheme of V_{15} as a function of the external field.

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2. Experimental results

The unit cell of V_{15} includes 8 molecules of crystal water and one water molecule inside the cluster [2]. The NMR spectrum consists of only one resonance line with the half-width of about 50 Oe. Figure 2 shows the temperature dependence of the relaxation rate in various applied fields. At the lowest field of 0.34T, $1/T_1$ was almost temperature independent down to 1.4K. In the fields between 1.3T and 1.85T, $1/T_1$ exhibits remarkable decrease with decreasing temperature. As the external field increases, $1/T_1$ decreases. The relaxation rate, however, exhibits a trend to increase around H_c. When the field exceeds H_c, $1/T_1$ becomes appreciably smaller. Such an experimental feature seems to reflect the energy scheme as given in Fig.1.(a). Figure 3 shows the field dependence of $1/T_1$ at 1.4K. We see anomalous increase around 0.3 and 2.9T.

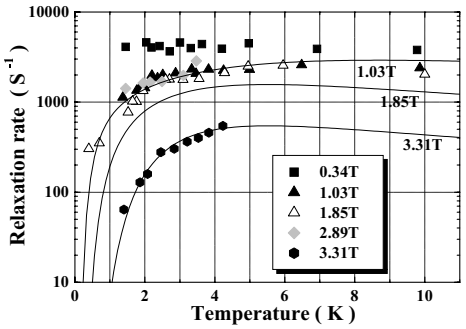

Fig. 2. Temperature dependencies of $1/T_1$ of ^{1}H in V_{15} at various external fields. The solid lines represent the result of the best fitting of eq.(2) in the text.

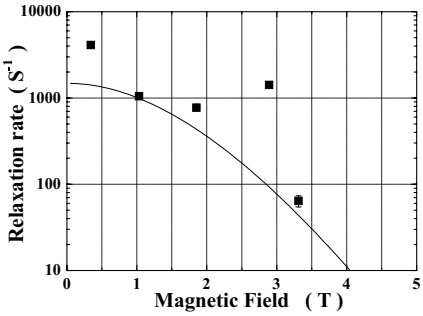

Fig. 3. Field dependence of $1/T_1$ of ^{1}H in V_{15} at 1.4K. The solid line represents the result of the best fitting of eq.(2) in the text.

3. Analysis and discussion

As in most multi-level system at relatively high temperatues, the spin-phonon interaction will play an important role in T_1 mechanism in the present case of V_{15}. As for the molecular cluster magnets, the proton and muon relaxations in $Mn_{12}Ac$ was interpreted by Lascialfari et al. from such a standpoint [3]. Now we tentatively consider only the fluctuation between the two levels in S=1/2 by considering the ground state and the excited state in S=1/2 configuration. We introduce the average life-times τ_0 and τ_1, which are expressed as $1/\tau_0 = C\Delta^3/\{\exp(\Delta/k_{\rm B}T)-1\}$ and $1/\tau_1 = C\Delta^3/\{1-\exp(-\Delta/k_{\rm B}T)\}$, where Δ is the energy difference given by $\Delta = g\mu_{\rm B}H_0/k_{\rm B}$ in K, and C is the coupling constant for the spin-phonon interaction [4]. Then the correlation function for the transverse fluctuating field at the protn site is calculated to be:

$$\langle\{\delta h_+(t)\delta h_-(0)\}\rangle = h_{\rm eff}^2 \exp(-\frac{t}{\tau_{\rm c}}) \qquad (1)$$

with $1/\tau_{\rm c} = 1/\tau_0 + 1/\tau_1$, and $h_{\rm eff}^2 = h_\perp^2 \tau_0\tau_1/(\tau_0+\tau_1)^2$, where $h_\perp$ is transverse fluctuating field appearing during the fluctuation. Considering the statistical weight for configuration of S=1/2, $1/T_1$ is given as:

$$\frac{1}{T_1} = \frac{(E_- + E_+)}{Z}(\gamma_{\rm N}h_\perp)^2 \frac{2\tau_{\rm c}}{1+(\omega_{\rm N}\tau_c)^2} \qquad (2)$$

where Z is partition function with respect to all levels for S=1/2 and 3/2, and E_- and E_+ are the Boltzmann factor for the relevant levels for S=1/2. The solid lines in Fig.2 and Fig.3 represent the result for the best fitting of the eq.(2) to the experimental results. This was obtained by choosing $h_\perp$=550 Oe. and $C \approx 1.2\times10^6$ (sec^{-1}K^{-3}). This value of C lies somewhat above the range of predicted value of $10^3 \sim 10^5$ for $Mn_{12}AC$ [3]. As we see, the agreement between the experiment and the theory is rather satisfactory. The temperature dependence of the relaxation rate at 0.3T may be due to the predominance of another relaxation process such as direct process, and the relaxation rate at 2.9T may be related to the level clossing between S=1/2 and S=3/2 configuration. These are the subject of future understanding.

References

[1] D. Gatteschi, L. Pardi, A. L.Barra, A. Müller, Molecular Engineering **3** (1993) 157

[2] I. Chiorescu, W. Wernsdorfer, A. Müller, H. Bogge, B. Barbara, Phys. Rev. Lett. **84** (2000) 3454

[3] A. Lascialfari, Z. H. Jang, F. Borsa, P. Carreta, D. Gatteschi, Phys. Rev. Lett. **81** (1998) 3773

[4] J. Villain, F. Hartmann-Boutron, R. Sessoli, A. Pettori, Euro. Phys. Lett. **27** (1994) 159