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^{1}H-NMR studies on spin dynamics in molecular nanomagnet V15

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Abstract

^{1}H-NMR study of a molecular magnet $K_6[V_{15}As_6O_{42}(H_2O)]8H_2O$ (in short, V15) provides evidences for a gradual slowing of fluctuations of the V^{4+} spins with increasing magnetic field. The temperature and magnetic field dependence of $1/T_1$ is well explained by a model in terms of spin phonon interaction in the magnetic field region ($H>2.7$ T) where the ground state of the V15 cluster is $S=\frac{3}{2}$. On the other hand, the T_1 data is not reproduced by the model in the low magnetic field region where the ground state is formed by two $S=\frac{1}{2}$ doubly degenerate states, suggesting importance of additional contribution to the spin dynamics of V^{4+} moments due to peculiarities of the $S=\frac{1}{2}$ triangle configuration in the V15 cluster.

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Keywords: NMR; Hyperfine interaction; Relaxation time; V15 cluster

1. Introduction

Recently much attention has been paid to nanoscale molecular magnets such as the so-called Mn12-ac [1,2] and Fe8 cluster [3,4] after the discovery of novel quantum phenomena of the quantum tunneling of magnetization. This exciting discovery has triggered interests in exploring quantum effects on magnetic properties of other molecular nanomagnets. In particular, $K_6[V_{15}As_6O_{42}(H_2O)]8H_2O$ (in short, V15) is considered to be an $S=\frac{1}{2}$ Heisenberg triangular system in which vanadium ions are arranged in a quasi-layered structure formed of a triangle sandwiched between two hexagons [5].

The V15 cluster consists of 15 V^{4+} ions with $S=\frac{1}{2}$. All exchange interactions between V^{4+} spins are antiferromagnetic (AF) [5]. Each hexagon of the cluster has three pairs of AF coupled

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spins with $J\sim-800$ K, showing nonmagnetism at low temperature [6,7]. Each spin of V^{4+} ions in the triangle is coupled with the spins in both hexagons with $J=-150$–-300 K, resulting in a very weak exchange interaction with $J\sim-2.44$ K between the spins within the triangle [8]. This pattern of couplings leads to a frustrated $S=\frac{1}{2}$ triangle system. The ground state is formed by two $S=\frac{1}{2}$ doubly degenerate states separated by a small gap of $\sim$0.2 K from a magnetization measurement [9]. The energy scheme is given by the ground state of $S=\frac{1}{2}$ and the excited state of $S=\frac{3}{2}$ which lies $T\sim3.8$ K above [10]. By the application of an external magnetic field, the ground state can be changed from two $S=\frac{1}{2}$ doubly degenerate states to an $S=\frac{3}{2}$ state at $H\sim2.7$ T [11].

In this paper, we report ^{1}H-NMR results in order to shed light from a microscopic point of view on the static and dynamical properties of the V^{4+} spins ($S=\frac{1}{2}$) on the triangle with change of ground states $S=\frac{1}{2}$ and $S=\frac{3}{2}$ by external field.

2. Experimental

Polycrystalline sample of V_{15} was prepared as described in Ref. [12]. Temperature (T-) dependence of magnetic susceptibility of the samples was very similar to the one reported previously [6,8]. The ^{1}H-NMR measurements were carried out using a phase-coherent pulse spectrometer. ^{1}H-NMR spectra were obtained by sweeping the magnetic field. Nuclear spin-lattice relaxation time, T_1, was measured by a saturation method with the frequency tuned at the highest peak position of ^{1}H-NMR spectrum. The nuclear magnetization recovery was found to be nonexponential, which is due to distribution of the nuclear relaxation process among magnetically-inequivalent protons. T_1 was obtained from an initial slope of the recovery curve [14]. The nuclear spin–spin relaxation time T_2 was determined by spin-echo decay curve.

3. Results

Fig. 1 shows several ^{1}H-NMR spectra measured at different frequencies at $T=1.5$ K. The observed

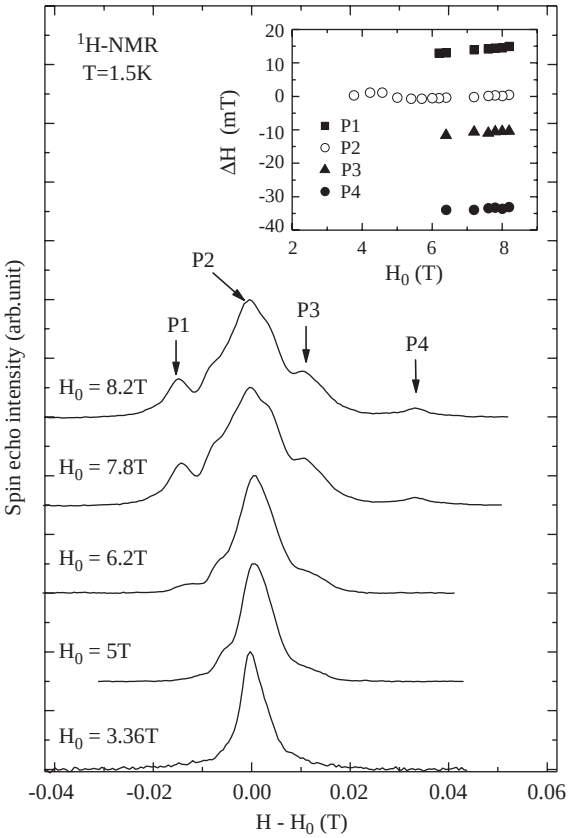

Fig. 1. ^{1}H-NMR spectra in the V15 powder sample at $T=1.5$ K with different resonance frequencies. The horizontal axis for each spectrum is shifted by the corresponding Larmor field H_0. The inset shows the H_0 dependence of $\Delta H=H_0-H_i$ where H_i is the magnetic field at each peak (P_i) at $T=1.5$ K.

^{1}H-NMR spectrum is narrow (a full-width of half amplitude (FWHA) of $\sim$30 Oe) below $H\sim2$ T. However, the spectrum with a single peak changes to the one with multipeak in the magnetic field for $H>5$ T. At least 4 peaks ($P1$–$P4$) are apparent in the spectrum at high magnetic field. The inset shows the difference between the applied field, H_0, and the resonance field H_i, ($\Delta H=H_0-H_i$) as a function of H_0 at each peak. The shifts for each peak are field independent, indicating that the shift arises from a spontaneous static field at the proton sites from a frozen V^{4+} spin configuration on the triangle. The internal fields at each proton site are estimated to be 140, $\sim$0, -108 and -335 Oe for $P1$, $P2$, $P3$ and $P4$, respectively.