NMR study of quantum spin liquid and its phase transition in the organic spin-1/2 triangular lattice antiferromagnet EtMe₃Sb[Pd(dmit)₂]₂

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Abstract. We found by ¹³C-NMR experiment that a quasi-two-dimensional organic antiferromagnet with spin 1/2 on the triangular lattice, EtMe₃Sb[Pd(dmit)₂]₂, has no classical magnetic ordering down to 19.4mK, although the magnetic exchange interaction J is 220-250K. The quantum spin liquid state is realized in this material due to the significant spin frustration and quantum fluctuation. The ¹³C nuclear spin-lattice relaxation rate T⁻¹ under an external magnetic field of 7.65T indicates that the excitations have no spin gap in this spin liquid phase above 1.0K. Then the relaxation rate exhibits a clear kink at 1.0K, and shows a steep decrease below this temperature proportional to T². This clearly shows a continuous phase transition at 1.0K and the steep decrease of the spin fluctuation could show the appearance of the excitation gap in the lower spin liquid phase. The power law but not exponential law of the temperature dependence may imply a nodal gap rather than a full gap.

1. Introduction

An antiferromagnet on the triangular lattice is the most fundamental geometrically frustrated magnet. The most simple example is an Ising type antiferromagnet on the triangular lattice, which has a macroscopic number of degeneracy in the ground state, and has no magnetic ordering even at zero temperature. For the Heisenberg type case the exotic resonating valence bond (RVB) state composed of a quantum mechanical superposition of singlet pairs has been proposed [1], and attracted much attention in the field of condensed matter physics also because of its relation to the possible origin for high temperature superconductivity. Now it is recognized theoretically, however, that the nearest neighbor Heisenberg antiferromagnet on the triangular lattice has a 120° spin ordered structure in the ground state for both classical and quantum spin systems. On these theoretical interests the real model materials for the triangular lattice antiferromagnet have been sought. Especially the spin 1/2 system is more attractive, as the quantum fluctuation would destroy the conventional magnetic ordering and is expected to give rise to a new quantum spin state. Recently we discovered that the organic compound EtMe₃Sb[Pd(dmit)₂]₂ (Et = C₂H₅, Me = CH₃, dmit = 1,3-dithiole-2-thione-4,5-dithiolate) is an ideal model material for the two dimensional antiferromagnet on the triangular lattice and realizes a quantum spin liquid state [2], as well as the organic compound of κ- (BEDT-TTF)₂Cu₂(CN)₃ (BEDT-TTF = bis(ethylendithio)-tetraethiafulvalene) [3].
In this paper, we report the discovery of a quantum spin-liquid state and its instability found in EtMe₃Sb[Pd(dmit)₂]₂ by means of ¹³C-NMR experiment down to 19.4mK [2] [4] [5].

A layered organic compound EtMe₃Sb[Pd(dmit)₂]₂ is a good candidate material for the quantum antiferromagnet on the triangular lattice, as shown in Fig. 1. The Pd(dmit)₂ molecules are strongly dimerized, and these dimers [Pd(dmit)₂]₂ form the nearly regular-triangular lattice and have spin s = 1/2. The magnetic [Pd(dmit)₂]₂ layers are separated by nonmagnetic layers of the closed-shell monovalent cation EtMe₃Sb, and thus the compound is considered to be a quasi two-dimensional magnet. The localized spins on the dimers interact antiferromagnetically with each other. The transfer integrals were calculated using the extended Hückel method to be 28.3, 27.7 and 25.8meV between the [Pd(dmit)₂]₂ dimers, while 453.5 meV for intradimer. Thus the three exchange interactions are nonequivalent but close to each other [6]. The exchange interactions are estimated to be 220–250K by the static susceptibility measurement and the high temperature expansion of the regular-triangular spin-1/2 Heisenberg antiferromagnet [7] [2] with a g-value of 2.038 obtained by ESR measurement [8]. The ambiguity of the value of exchange interaction may be attributed to the approximation of a regular-triangular lattice and/or an existence of higher-order exchange interactions.

Figure 1. (a) Pd(dmit)₂ molecule with enriched ¹³C isotope at both ends of the molecule. (b) Crystal structure of a [Pd(dmit)₂]₂ layer. Two Pd(dmit)₂ molecules are dimerized. (c) Schematic of the spin system of EtMe₃Sb[Pd(dmit)₂]₂, where circles represent [Pd(dmit)₂]₂ dimers with localized 1/2 spins.

2. Experimental method
Fine high-quality single crystals of EtMe₃Sb[Pd(dmit)₂]₂ were synthesized by an aerial oxidation method. The typical sizes were of 0.3mm×0.3mm×0.01mm. For the ¹³C-NMR measurements, the carbon atoms at both ends of the Pd(dmit)₂ molecules were enriched with ¹³C isotopes, as shown in figure 1(a). A large number of the single crystals were packed into a glass tube with random orientation. The ¹³C-NMR measurements were performed from 300K to 19.4mK under a magnetic field of 7.65T. The NMR spectra were obtained by Fourier transformation of spin echo signals refocused after the π/2 - π pulse sequence. The typical pulse widths of π/2 and π were 3 and 6µs, respectively. The inverse of these values were sufficiently larger than the present spectral widths, and thus the pulses could cover the whole NMR spectra. The spin-lattice relaxation rate T⁻¹ was obtained from the recovery curve of the integrated spin-echo intensity M(t) after time delay t from saturation comb pulses.

3. Experimental results and discussions
Figure 2 shows the ¹³C-NMR spectra of EtMe₃Sb[Pd(dmit)₂]₂. The shape of the spectra scarcely changes, and the critical broadening of the spectrum, which is characteristic of spin freezing, was not observed in the whole temperature range from 272K to 19.4mK. The observed local static field, which is estimated from the width of the spectrum, is too small even at lowest temperature to be understood as a magnetic long range ordering or a spin glass state. The spectral tail is at most within
50kHz, which is much smaller than the scale of the hyperfine coupling constant discussed later. This result indicates that EtMe$_3$Sb[Pd(dmit)$_2$]$_2$ does not undergo either spin ordering or freezing down to 19.4mK, which is 1/10,000 of the exchange interaction $J$. Therefore we can conclude that a quantum spin liquid state is realized in this material. A very small broadening of the spectra at low temperatures is attributed to an inhomogeneous broadening due to slight static local fields [2]. This small inhomogeneous broadening is also observed in the other spin liquid material κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ [3], and thus is considered to be a universal nature of these spin liquids, which are expected to have considerably long-range spatial spin correlation.

![Figure 2. Temperature variation of $^{13}$C-NMR spectra of EtMe$_3$Sb[Pd(dmit)$_2$]$_2$ at 7.65T.](image)

The temperature dependence of the $^{13}$C nuclear spin-lattice relaxation rates $T_1^{-1}$ at an external magnetic field of 7.65T is shown in figure 3. The recoveries of the $^{13}$C nuclear magnetization $M(t)$ were not single exponential at some temperature region, but could be expressed by the stretched exponential function in the whole experimental temperatures as,

$$
\frac{M(\infty) - M(t)}{M(\infty)} = \exp\left(-\left(\frac{t}{T_1}\right)^{\beta}\right),
$$

where $\beta$ is the stretching exponent. The stretching coefficient $\beta$ generally denotes the degree of inhomogeneity of the spin system, while the nuclear magnetization in the homogeneous system relaxes exponentially with $\beta=1$. The temperature dependence of the obtained coefficient $\beta$ is shown in figure 4. In figure 3, we also show the relaxation rate determined from an initial decay of the recovery curve. The relaxation rate derived from the initial decay gives the average value among different relaxation rates. The difference between the two relaxation rates shows the degree of inhomogeneity.

The rate $T_1^{-1}$ gradually decreases as temperature decreases from 300K. The rate $T_1^{-1}$ stops decreasing and has a finite value between 5 and 1K. Then a steep decrease is observed below 1.0K with a kink.

First, we consider the spin dynamics at high temperatures. We can evaluate the antiferromagnetic spin correlations by comparing $T_1^{-1}$ with the static spin susceptibility $\chi$. The spin-lattice relaxation rate
is the NMR frequency $\omega_n$ component of Fourier transformation of the time-autocorrelation function of the fluctuating transverse local field $\delta H^\pm(t)$ at nuclear sites as,

$$T_1^{-1} = \frac{\gamma_n^2}{2} \int_{-\infty}^{\infty} dt \left\{ \langle \delta H^-(t) \delta H^+(0) \rangle \right\} \exp(-i\omega_n t), \quad (2)$$

where $\gamma_n$ is the gyromagnetic ratio of nuclear spin. The fluctuating local field at nuclear sites comes from the fluctuation of electron spins through the hyperfine interaction, and the contributing spin correlation function is related to the static susceptibility $\chi'(q, \omega = 0)$ owing to the fluctuation-dissipation theorem [9]. For the high-temperature paramagnetic state where the spin autocorrelation

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**Figure 3.** Temperature dependence of relaxation rate $T_1^{-1}$. The horizontal axis is logarithmic in figure (a), while it is linear in figure (b). The blue circles indicate the values determined from the stretched-exponential analysis, and the red squares denote the values determined from the initial decay of recovery curves. An orange solid curve shows values calculated using $3.6 \text{ (mol emu}^{-1} \text{K}^{-1} \text{s}^{-1}) \times \chi T$ for the relaxation rate in the paramagnetic fluctuation at high temperatures. The green solid line denotes the temperature dependence proportional to $T^2$ in the lower quantum spin liquid phase.

**Figure 4.** Temperature dependence of stretching exponent $\beta$ in the recovery curve fitted to equation (1).
function decays exponentially with time, the rate is derived as

\[ T_1^{-1} \propto T \sum_q \frac{\chi'(q,0)}{\Gamma_q}, \]  

(3)

where \( \chi(q,\omega) = \chi'(q,\omega) + i\chi''(q,\omega) \) is the dynamic spin susceptibility and \( \Gamma_q \) is the decay rate of the autocorrelation function. At sufficiently high temperatures \( (T \gg J) \) we can also assume that the autocorrelation function has no \( q \)-dependence due to random fluctuation, and is equal to the static susceptibility, i.e. \( \chi'(q,0) = \chi' \). So the temperature dependence of \( T_1^{-1} \) in the paramagnetic region can be described as [10]

\[ T_1^{-1} \propto \chi T. \]  

(4)

The calculated values using the experimental susceptibility are shown by the orange solid lines in figure 3(a) and (b). The calculated curve agrees well with the experimental data above 180K, as is clearly found in figure 3(b). Thus, antiferromagnetic correlations are almost absent around room temperature. The proportionality coefficient in equation (4) is 3.6 mol emu\(^{-1}\) K\(^{-1}\) s\(^{-1}\), which gives a hyperfine coupling constant to be \( 9 \times 10^2 \) kHz/\( \mu_B \) by assuming Gaussian fluctuation [10] and by using an exchange frequency \( \omega_{\text{ex}} = 5 \times 10^{13} \) rad/ s, which is calculated from the exchange \( J = 220–250K \) and the neighboring number \( z = 6 \). This hyperfine value is consistent with our previous estimation of several hundreds of kHz/\( \mu_B \) [11], which was calculated on an analysis of the spectral width.

The experimental data is, however, enhanced from the \( \chi T \) line below 180K, which corresponds to the energy of \( J \). The substantial deviation of the experimental \( T_1^{-1} \) data suggests the development of the antiferromagnetic spin correlations, because it indicates an enhancement of \( \chi'(q, 0) / \chi'(0, 0) \) and a slowing down of \( \Gamma_q \) at a specific \( q \).

The relaxation rate \( T_1^{-1} \) smoothly decreases down to 1K without any features of the spin ordering or freezing, and has a finite value between 5 and 1K, as is shown in figure 3(a). This temperature dependence indicates that this system does not have an appreciable spin gap. The paramagnetic state remains in spite of the development of antiferromagnetic correlation from much higher temperatures around 180K. Since 1K is lower than 1% of \( J \), thermal fluctuations are negligible in this temperature region. Thus, the absence of spin ordering or freezing is attributed not to thermal fluctuations but to quantum fluctuations. Considering the absence of an appreciable spin gap, this state is clearly distinct from the VBS state accompanied by the spin dimerization. Therefore, we can conclude that this state is regarded as the quantum spin-liquid state with no spin gap above the temperature of 1.0K.

The temperature dependence of the relaxation rate \( T_1^{-1} \) shows an obvious kink at around 1.0K, as is found in figure 3(a). This strongly suggests that a phase transition occurs at this temperature. This transition is not a first-order but a continuous transition, as no discontinuous jump is observed in the temperature dependence of \( T_1^{-1} \). The continuous phase transitions always accompany changes of states, that is symmetry breaking and/or topological ordering. Therefore, our result indicates that the gapless spin liquid changes to a different spin state accompanying symmetry breaking and/or topological ordering. This transition is not a classical magnetic ordering or freezing, because the anomaly in \( T_1^{-1} \) is not a critical divergence and also the NMR spectrum shown in figure 2 has no broadening below this temperature.

The relaxation rate \( T_1^{-1} \) in the lower temperature phase below 1.0K shows a steep decrease, as is found in figure 3(a). The stretching coefficient \( \beta \) decreases to 0.5 around the transition temperature, and returns gradually to 1.0 at lower temperatures, as shown in figure 4, that is, the recovery curves of nuclear magnetization return to single exponential functions at sufficiently low temperatures. This temperature dependence suggests that the distribution of \( T_1^{-1} \) is amplified by the slight imperfections in the sample and the increase of the correlation length in the vicinity of the phase transition of this quantum spin liquid.
The rate $T^{-1}_1$ in the lower temperature phase is clearly proportional to $T^2$. This is in contrast to the nature of the fully gapless spin liquid with the spinon Fermi surface, where $T^{-1}_1 \propto T$ for a Fermi-liquid case or diverges for a non-Fermi-liquid case. Thus, the low temperature phase is not fully gapless, and has a spin gap at least in some portion of $q$-space as a nodal gap, which is similar to superconducting gaps in anisotropic superconductors.

4. Conclusion
In conclusion, our $^{13}$C-NMR experiments show that the $s = 1/2$ Heisenberg antiferromagnet on the triangular lattice EtMe$_3$Sb[Pd(dmit)$_2$]$_2$ does not undergo classical spin ordering or freezing down to 19.4mK, which is less than $1/10,000$ of the exchange interaction $J$. While this quantum spin liquid has a gapless spin excitation above 1.0K, we found clear evidence that the spin system under 7.65T shows an instability other than classical ordering at around 1.0K and has a spin gap below this temperature. This gap may be nodal similar to that in anisotropic superconductors.

Quantum liquids of $^3$He, $^4$He and electrons in metals exhibit exotic phase transitions with the symmetry breaking as superfluidity and superconductivity. Various attractive predictions for instability or transition in the quantum spin liquid have been proposed theoretically, such as the spinon pairing [12][13][14], chiral RVB [15] [16], $Z_2$-vortex [17] and spin nematic [18]. Our discovery of the transition in EtMe$_3$Sb[Pd(dmit)$_2$]$_2$ is expected to provide important information on a new instability of the quantum spin liquid.

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