Ground state of the organic spin-liquid material
EtMe$_3$Sb[Pd(dmit)$_2$]$_2$

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Abstract. The organic Mott insulator EtMe$_3$Sb[Pd(dmit)$_2$]$_2$ is a 1/2-spin system on a nearly-
regular triangular lattice. It does not show classical antiferromagnetic ordering in spite of strong
antiferromagnetic exchange interactions $J = 220$–$250$ K, and thus it is regarded as a spin liquid
material. We have found that $(T/T_1)^{-1}$ of this spin liquid state shows a peak at around $1$
K and after that $(T/T_1)^{-1}$ decreases on cooling. This is not attributed to slowing down of
the spin dynamics because $T_2^{-1}$ does not show any enhancement down to low temperature
limit. Therefore, the decrease of $(T/T_1)^{-1}$ is attributed to disappearance of spin excitations,
suggesting that magnetic excitations acquire an energy gap at least in some portion of $q$-space.
This indicates that the ground state of the present spin-liquid material is not a state with spinon
Fermi surface, where magnetic excitations are fully gapless and thus $(T/T_1)^{-1}$ does not decrease
down to low temperature limit.

1. Introduction
Quantum spin liquid state, where spins are vital but does not show classical magnetic ordering
even at absolute zero temperature due to quantum fluctuations, has been a long-sought state of
matter. Although it was theoretically proposed early on that this state may be realized in 1/2-
spin systems on frustrated lattices [1], this state was not experimentally found for many years.
This is because real model materials of ideal frustrated 1/2-spin systems were limited. Recently,
however, some organics are recognized as ideal frustrated 1/2-spin systems, and the spin-liquid
state has been found in two triangular-lattice antiferromagnets, $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$
(BEDT-TTF = bis(ethylenedithio)-tetrathiafulvalene) [2] and EtMe$_3$Sb[Pd(dmit)$_2$]$_2$ (dmit =
1,3-dithiole-2-thione-4,5-dithiolate, Me = CH$_3$, Et = C$_2$H$_5$) [3].

Stimulated by these experimental findings, theorists have discussed the nature of the quantum
spin liquid on triangular lattices. This is a profound topic, and there are many different ideas
and theories which have proposed so far. Under this circumstance, further experimental studies
of the spin liquid state on triangular lattices are highly desired, to develop understanding of
the spin liquid physics on the triangular lattice. One of the important points to understand
the spin-liquid state is what kind of fluctuations and excitations the state has. We have been
performing experiments for the spin liquid material EtMe$_3$Sb[Pd(dmit)$_2$]$_2$, aiming to understand
this point.

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The family of layered organic salts $X\text{[Pd(dmit)}_{2}]_{2}$ ($X$: nonmagnetic monovalent counter cation) have scalene-triangular lattices of $[\text{Pd(dmit)}_{2}]_{2}$ dimers, as shown in Figs. 1 and 2. They are Mott insulators and thus have a localized 1/2 spin on each dimer [4]. Therefore, they are triangular-lattice spin systems. Among them, $\text{EtMe}_3\text{Sb}[\text{Pd(dmit)}_{2}]_{2}$ is a nearly regular-triangular spin system, because the interdimer transfer integrals between the localized orbitals along the three directions of the triangles are close to each other [3].

The exchange interactions of $\text{EtMe}_3\text{Sb}[\text{Pd(dmit)}_{2}]_{2}$ between neighboring spins along the three directions were estimated to be 220-250 K from magnetic susceptibility data [3]. In spite of the strong exchange interactions, we found from $^{13}$C-NMR (nuclear magnetic resonance) measurements that this material does not undergo classical antiferromagnetic ordering down to at least down to 19.4 mK, which is the lowest stable temperature achieved using our dilution refrigerator and is less than 0.01 % of the exchange interactions [5, 6].

Importantly, we have also discovered that temperature dependence of the spin-lattice relaxation rate of $^{13}$C-NMR shows an obvious kink at around 1 K and the rate shows a rapid decrease below this temperature.

We discuss the low-temperature phase of this spin system in this report.

2. Experimental method

We prepared fine high-quality single crystals of $\text{EtMe}_3\text{Sb}[\text{Pd(dmit)}_{2}]_{2}$ with typical sizes of 0.3 mm × 0.3 mm × 0.01 mm, using an aerial oxidation method. For the $^{13}$C-NMR measurements, the carbon atoms at both ends of the $\text{Pd(dmit)}_{2}$ molecules were enriched with $^{13}$C isotopes, as shown in Fig. 3. The NMR measurements were carried out at a field of 7.65 T using many single crystals with no particular orientation packed into a glass tube. The NMR spectra were obtained by Fourier transformation of spin-echo signals refocused after the pulse sequence of $\pi/2 - \tau - \pi$, where $\tau$ was the rf pulse interval. The typical pulse widths of $\pi/2$ and $\pi$ were 3 and 6 $\mu$s, respectively. These values were sufficiently smaller than the inverse of the spectral widths, and thus the pulses could cover the whole NMR spectra. The spin-spin relaxation ($T_{2}^{-1}$) curves were obtained from the integrated spin-echo spectral intensity $M(2\tau)$ with varying $\tau$. The spin-lattice relaxation ($T_{1}^{-1}$) curves were obtained from the spin-echo spectral intensity $M(t)$ after
time delay \( t \) following saturation comb pulses. The spin-lattice relaxation time \( T_1 \) in this report is determined from the stretched-exponential analysis [6]. The spin-spin relaxation time \( T_2 \) is defined as the time when the recovery curve of \( M(2\tau) \) reaches \( 1/e \).

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S=^{13}\text{C} \quad \big| \quad \text{Pd} \quad \big| \quad S=S=^{13}\text{C}
\]

**Figure 3.** Pd(dmit)\(_2\) molecule with selective substitution of \(^{13}\text{C}\) isotope. The carbon atoms at both ends of the molecule are enriched.

### 3. Result and Discussion

Figure 4 shows the temperature dependence of the spin-lattice relaxation rate multiplied by the inverse of temperature \((T)\). It shows a clear kink at around 1 K, below which \((T_1 T)^{-1}\) decreases on cooling. The value \((T_1 T)^{-1}\) measures the imaginary part of the spin susceptibility \(\sum_q \chi''(q, \omega_N)/\omega_N\), where \(q\) is wavenumber and \(\omega_N\) is the NMR frequency (in the present case, \(\omega_N = 81.8\) MHz). We explained in a previous report [6] that this decrease of \((T_1 T)^{-1}\) is due to a decrease of spin excitations and thus due to a spin gap formation.

Some people may think that the present decrease of \((T_1 T)^{-1}\) might be attributed to the other scenario, that is, slowing-down scenario as follows. If the characteristic frequency of the spin dynamics \(\Gamma\) would decrease beyond NMR frequency on cooling, \((T_1 T)^{-1}\) would be expected to decrease on cooling after showing a peak. The present material is a quasi-two-dimensional system, and thus, they may think that, the present material might show slowing down of \(\Gamma\) toward around zero temperature, because the Mermin-Wagner theorem guarantees that pure-two-dimensional Heisenberg spin systems can undergo magnetic ordering only at absolute zero temperature, even though the ground state is a magnetically-ordered state.

However, this slowing-down scenario is not the case in the present material. We explain this point.

The linewidth of NMR spectrum reflects the sum of the three fields which nuclear spins experience: static inhomogeneous field, slowly fluctuating (particularly, on the order of kHz) field from electron spins, and field from other nuclear spins. If \(\Gamma\) decreased far beyond the NMR frequency of the order of MHz and reached around the order of kHz, the \(^{13}\text{C}\)-NMR linewidth would increase toward the scale of the hyperfine coupling constant, which is about \(9 \times 10^2\) kHz/\(\mu_B\) [3, 7], due to growth of slowly fluctuating field. However, experimental results reported in Ref. [6] show that the \(^{13}\text{C}\)-NMR linewidth does not broaden (remains within \(~50\) kHz) down to 19.4 mK, which is much lower than the peak temperature of 1 K. That is, the \(^{13}\text{C}\)-NMR linewidth shows no sign of slowing down of spin dynamics. This is one evidence that can deny the slowing-down scenario.

Spin-spin relaxation rate, \(T_2^{-1}\), is a quantity which is more sensitive than the spectral linewidth to detect slowly fluctuating field, because \(T_2^{-1}\) is not affected by static inhomogeneous field in contrast to the spectral linewidth. This value probes only the two fields: slowly fluctuating field from electron spins and field from other nuclear spins. Figure 5 shows the temperature dependence of \(T_2^{-1}\) of EtMe\(_3\)Sb[\(\text{Pd(dmit)}_2\)]\(_2\). The observed values of \(T_2^{-1}\) correspond to about 1 kHz, which is much smaller than the spectral linewidth of about 50 kHz. This means that the spectral linewidth is mainly dominated by static inhomogeneous field. The rate \(T_2^{-1}\) is not affected by it and thus is a much better quantity to check for the slowly fluctuating field. Importantly, we can see that \(T_2^{-1}\), as well as the spectral linewidth, shows no enhancement down to low temperatures, retaining an almost constant value. This is a strong
evidence for absence of slowly fluctuating field and thus we conclude that the slowing-down scenario is not the case in the present material. The constant value of $T_2^{-1}$ is well accord with contribution of the dipole field from other nuclear spins. The nuclear dipole field makes the dominant contribution to $T_2^{-1}$ in the present material because strong slowly-fluctuating field is absent.

Therefore, we can conclude that the decrease of $(T_1 T)^{-1}$ below 1 K does not mean the slowing down of the spin dynamics. The behaviors of the spectral linewidth and $T_2^{-1}$ guarantee that the spin dynamic does not undergo serious slowing down, and thus the decrease of $(T_1 T)^{-1}$ simply indicates a decrease of the spin excitations, as discussed in the previous report [6].

Our finding, the decrease of the spin excitations, denies the picture of the fully gapless spin-liquid state with spinon Fermi surface, where $(T_1 T)^{-1}$ remains constant (Fermi-liquid case) or diverges (non-Fermi-liquid case) on cooling. Figure 4 means that the imaginary part of the spin susceptibility vanishes on approaching zero temperature and thus the ground state has a spin gap at least in some portion of $q$-space. In addition, the decrease of $(T_1 T)^{-1}$ does not follow an exponential law but a power law in temperature. This result implies the possibility that the spin gap is a nodal one.

Here we comment on a few concerns about our NMR data, which some people might have. One concern is that the NMR spin-lattice relaxation might be affected by impurities. Such impurities, if any, are few and thus generally only slightly influence the relaxation. However, in a spin-gapped system, a spin gap causes the intrinsic relaxation to be so small at low temperatures that the slight relaxation caused by the impurities might become detectable. In such cases, $(T_1 T)^{-1}$ might not reflect the intrinsic spin dynamics. Another concern is that, in the present system, the counter nonmagnetic cation EtMe$_3$Sb has low-energy molecular motion. The ethyl group and methyl group of the cation EtMe$_3$Sb shows quantum rotation, which survives even at low temperatures. This molecular motion does not affect the spin state because the motion exists not on the magnetic layer but on the nonmagnetic counter cation layer. However, it might...
affect physical quantities such as the NMR relaxation rates and thermodynamic quantities. In this context, it is important to confirm the reliability and reproducibility of the NMR data, and to obtain a guarantee that the present behavior of \((T_1 T)^{-1}\) shown in Fig. 4 definitely reflects the intrinsic spin dynamics of the present system. We have performed several experiments to check these points and succeeded in getting good reliability and reproducibility. We will report it elsewhere in the near future.

Lastly, we discuss the recently published data on the thermal conductivity \(\kappa\) of the present material by M. Yamashita et al [8]. They measured \(\kappa\) down to about 100 mK and found that \(\kappa/T\) seems to retain a nonzero value in the zero temperature limit. This reminds us of metal-like excitations. In contrast, our results deny the fully gapless spin-liquid state with spinon Fermi surface. We do not have a conclusive idea to reconcile this seeming contradiction, but here comment on one point. One clue may be the fact that, NMR relaxation rates probe only magnetic excitations, while thermal quantities probe both magnetic and nonmagnetic excitations. This difference may be the reason why observations look seemingly different between our NMR data and their thermal-conductivity data. Our NMR data does not provide any information on nonmagnetic excitations, which do not contribute to the dynamic spin susceptibility. The thing that can be definitively determined from our NMR data is that magnetic excitations have an energy gap at least in some portion of \(q\)-space in the ground state of \(\text{EtMe}_3\text{Sb}[\text{Pd(dmit)}_2]_2\).

4. Conclusion
We measured the spin-lattice relaxation rate \(T_1^{-1}\) and spin-spin relaxation rate \(T_2^{-1}\) of the organic spin-liquid material \(\text{EtMe}_3\text{Sb}[\text{Pd(dmit)}_2]_2\) at ultra-low temperatures. We found that \((T_1 T)^{-1}\) shows a peak at around 1 K and after that it decreases on cooling. This is not attributed to slowing down of the spin dynamics, because \(T_2^{-1}\) does not show any enhancement at low temperatures. The decrease of \((T_1 T)^{-1}\) indicates the disappearance of the spin excitations and thus indicates the appearance of a gap structure (at least in some portion of \(q\)-space) in magnetic excitations.

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