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Spin-liquid state in an organic spin-1/2 system on a triangular lattice, EtMe₃Sb[Pd(dmit)₂]₂

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Abstract

The series of [Pd(dmit)₂] salts (dmit = 1,3-dithiole-2-thione-4,5-dithiolate) is a Mott insulator on an anisotropic triangular lattice and has an antiferromagnetic exchange constant $J \sim 200$ K. While it has been revealed that most of them undergo antiferromagnetic transitions, the nature of the spin state of EtMe₃Sb[Pd(dmit)₂]₂ which has a nearly isotropic triangular lattice is still unknown. We investigated the spin state by means of ^{13}C NMR measurements down to 1.37 K for polycrystalline samples in which the carbon atoms in both ends of the Pd(dmit)₂ molecule were selectively enriched with the ^{13}C isotope. Both behaviours of the spin–lattice relaxation rate and the spectra indicate no spin ordering/freezing at least down to 1.37 K, which is lower than one-hundredth of the exchange interaction. Furthermore, the spin–lattice relaxation rate does not show an exponential temperature dependence and seems to retain a finite value at low temperatures. Thus, the ground state of this system is possibly the almost-gapless spin-liquid state.

1. Introduction

Quantum fluctuations have a destabilizing effect on the Néel state which is inevitably realized in the ground state of the classical antiferromagnetic system. In particular in a frustrated system, the quantum fluctuations work strongly and as a result may be able to destroy the Néel state so as to realize the quantum spin-liquid state where spin ordering/freezing is absent even at zero temperature. This possibility was proposed for the first time for the triangular spin-1/2 system [1]. Thus, the quantum spin system on a triangular lattice has attracted a great number of researchers, and many theoretical studies have been conducted [2–9]. However, only a few candidates of the real model materials are known [10–14] and thus the ground-state nature of the triangular spin-1/2 system is still an open question.
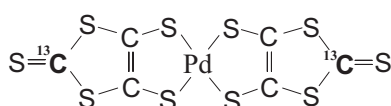
Figure 1. [Pd(dmit)$_2$] molecule with selective substitution of ^{13}C isotope. The carbon atoms at both ends of the molecule are enriched.

The series of [Pd(dmit)$_2$] salts, where dmit stands for 1,3-dithiole-2-thione-4,5-dithiolate, has an anisotropic triangular lattice structure of the [Pd(dmit)$_2$]$_2$ dimers. They are Mott insulators at ambient pressure, so a localized 1/2 spin exists on each dimer [15]. It has been shown that the finite-temperature magnetic behaviour of these spin systems is well explained by the spin-1/2 antiferromagnetic Heisenberg model on the triangular lattice with $J \sim 200$ K [15–17]. Most of them undergo Néel ordering as a result of the small spatial anisotropy of J [15–17]. On the other hand, the systems near the isotropic triangular lattice show unconventional ground states, such as the spin-gapped one, with or without charge separation [17–22]. EtMe$_3$Sb[Pd(dmit)$_2$] also has a nearly isotropic triangular lattice. The susceptibility χ of this salt is 5×10^{-4} emu mol^{-1} at 300 K, and it gradually increases to form a broad maximum with 6×10^{-4} emu mol^{-1} around 50 K on cooling [23]. As the temperature is further lowered, χ decreases but seems to remain at a finite value of about 4×10^{-4} emu mol^{-1} for $T \rightarrow 0$. Although this behaviour implies neither the spin gap nor the magnetic order, the slight contribution of the impurity Curie term prevents an unambiguous conclusion from being drawn about the spin state at low temperatures. Therefore, it is desired to perform NMR measurements for this salt, which can directly investigate the spin state.

2. Experimental details

The carbon atoms at both ends of the Pd(dmit)$_2$ molecule were enriched with ^{13}C isotope, as shown in figure 1. Fine single crystals of EtMe$_3$Sb[Pd(dmit)$_2$]$_2$ were prepared by an aerial oxidation method. We performed ^{13}C NMR measurements for a large number of the single crystals packed into a glass tube without any orientation. The observed spectra are, thus, powder patterns. The measurements were done in the temperature range between 272 and 1.37 K under an applied field of 7.65 T. The spectra were obtained by the Fourier transformation of the echo signals following the spin-echo $\pi/2$–π pulse sequence. The typical duration of the $\pi/2$ pulse was 1.5–2 μs. The spin–lattice relaxation rate, T_1^{-1}, was obtained from the recovery curve of the integrated spin-echo intensity. Since the recovery curve becomes curved at low temperatures, in this paper we tentatively define T_1 as the time when the recovery curve reaches $1/e$.

3. Results

Figure 2 shows the temperature dependence of ^{13}C NMR spectra under 7.65 T applied field. At high temperatures, we observed sharp spectra which have asymmetric shapes with shoulder structures. These shapes are explained by the cooperative effect of the nuclear–nuclear dipolar interaction and the powder distribution in the system with a uniaxial hyperfine coupling. At low temperatures, the spectrum gradually broadens as the temperature is decreased.

The temperature dependence of T_1^{-1} is shown in figure 3. The relaxation rate is about 0.5 s^{-1} at room temperature and it monotonically decreases with lowering temperature. It seems that it reaches a constant value at low temperatures, which contrasts with the exponential temperature dependence in a spin-gapped system.
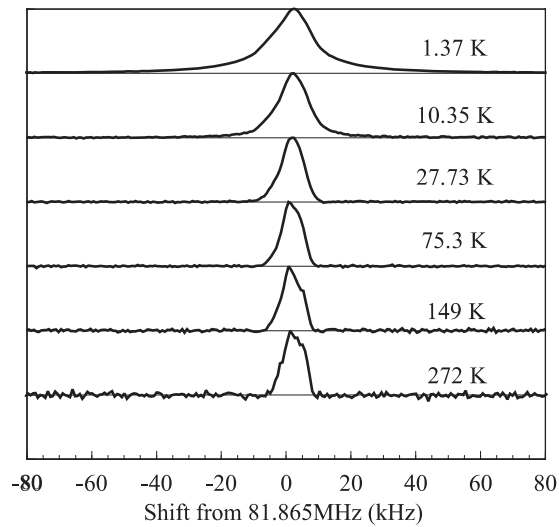
Figure 2. ^{13}C NMR spectra of polycrystalline samples of EtMe$_3$Sb[Pd(dmit)$_2$]$_2$ under a field of 7.65 T at different temperatures.
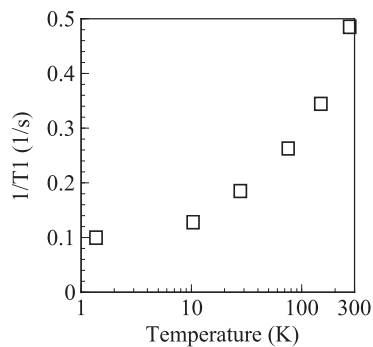
Figure 3. ^{13}C nuclear spin–lattice relaxation rate T_1^{-1} for polycrystalline samples under a field of 7.65 T.

4. Discussion

As shown in figure 3, T_1^{-1} does not show any critical enhancement which indicates the critical slowing down of the spin fluctuations. This suggests the absence of spin ordering/freezing down to 1.37 K, which is lower than one-hundredth of the exchange interaction. Furthermore, T_1^{-1} does not show an exponential temperature dependence and seems to retain a finite value at low temperatures, which suggests that there exists no significant spin gap more than 1 K in this system. In order to confirm the absence of the spin ordering/freezing, the hyperfine-coupling constant and the spectra are analysed in the following paragraphs.

The value of T_1^{-1} at room temperature is about 0.5 s^{-1}, which is two orders of magnitude smaller than that for the κ-(BEDT-TTF)$_2$X family such as κ-(BEDT-TTF)$_2$Cu$_2$CN$_3$ which is also a triangular antiferromagnetic spin-1/2 system. Its exchange interaction is 250 K [12], which is almost the same value as that for EtMe$_3$Sb[Pd(dmit)$_2$]$_2$. In a higher-temperature region than the energy scale of the exchange interaction, the spin dynamics

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generally depends only on the energy scale while it is not sensitive to the detail of the configuration of the exchange interaction. Thus, at room temperature, κ-(BEDT-TTF)$_2$Cu$_2$CN$_3$ should have the same spin dynamics as that of EtMe$_3$Sb[Pd(dmit)$_2$]$_2$. The difference in T_1^{-1} of the two system is, therefore, attributed to the difference in the hyperfine coupling constants. As T_1^{-1} is proportional to the square of the hyperfine coupling constant, the constant for EtMe$_3$Sb[Pd(dmit)$_2$]$_2$ must be one order of magnitude smaller than that for κ-(BEDT-TTF)$_2$X [24, 25] and is estimated to be several hundreds of kHz/μ_B. This value is consistent with the spectrum shapes at high temperatures which have shoulder structures in the frequency region about 5 kHz above the maximum peaks. The hyperfine coupling tensor K for the ^{13}C atom in the organic charge-transfer salts can be approximated by the uniaxial one, that is $K = (K^{xx}, K^{yy}, K^{zz}) = (-\alpha/2 + \beta, -\alpha/2 + \beta, \alpha + \beta)$ [26], where α is an anisotropic term which contributes to the spectrum structure for powder samples while β is an isotropic term which produces a shift of the first moment of the spectrum. Although the chemical shift could also contribute to the structures, the α value of several hundreds of kHz/μ_B reproduces the observed structures at high temperatures by taking into consideration the fact that the spin susceptibility at room temperature is about 5×10^{-4} emu mol^{-1} [23]. As for the isotropic term β, the value should not be more than a few hundreds of kHz/μ_B because no significant shift of the first moment of the spectra was observed within the experimental uncertainty of 1 kHz. Thus, the components of the hyperfine coupling constant are concluded to be several hundreds of kHz/μ_B.

In the high-temperature region, the spectra are sharp and their linewidths are explained by a convolution of the structure by the anisotropic hyperfine coupling mentioned above and Gaussian broadening by the nuclear–nuclear dipolar interaction. Thus, the system is in the paramagnetic state where all the [Pd(dmit)$_2$]$_2$ dimers have uniform small magnetizations which correspond to the susceptibility. At low temperatures, the spectrum gradually broadens as the temperature is decreased. Since the spin susceptibility decreases on cooling in the low-temperature region [23], this broadening cannot be explained by the uniform magnetization. Indeed, the structure caused by the anisotropic hyperfine coupling is overwhelmed, which suggests the appearance of an internal magnetic field beyond the field due to the uniform magnetization. Generally this type of broadening is observed in the spin-ordering/freezing state such as the Néel state or the spin-glass state where each site feels different large internal magnetic field caused by the ordering/freezing spin moments. However, the broadening in this system is so small that the system cannot be regarded as the spin-ordering/freezing state. While the dominant fraction of the spectra stays at the centre with little shift, only a minor fraction forms a tail of the spectra and contributes to the broadening. The broadening of the tail is at most within ± 50 kHz, which corresponds to about 0.1 μ_B according to the estimation of the coupling constant mentioned above. Thus, even if the broadening is assumed to be caused by the magnetic moments, they are not more than ~ 0.1 μ_B and they exist only on a small minority of the [Pd(dmit)$_2$]$_2$ dimers. The states at low temperatures, therefore, are not considered to be the spin-ordering/freezing states such as the Néel state or the spin-glass state.

As described above, the analysis of the spectrum confirmed the absence of the spin ordering/freezing at least down to 1.37 K. Since this temperature is lower than one-hundredth of the exchange interaction, the thermal fluctuations hardly exist at all in this temperature region. Thus, the absence of the spin ordering/freezing is probably attributed not to the thermal fluctuations but to the quantum fluctuations. It is, therefore, concluded that the quantum spin-liquid state is likely to be realized in this system. Considering the absence of the exponential temperature dependence in T_1^{-1}, the ground state of this system is possibly gapless spin liquid or ultrasmall-gapped spin liquid.

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5. Conclusion

We performed ^{13}C NMR measurements for a spin-1/2 system on a triangular lattice, EtMe$_3$Sb[Pd(dmit)$_2$]$_2$. The spectrum and T_1^{-1} did not show any feature of the spin ordering/freezing down to 1.37 K, which is lower than one-hundredth of the exchange interaction. In addition, T_1^{-1} keeps a finite value at low-temperature limit, which is contrasted with the exponential temperature dependence in a spin-gapped system. This means that the gap of this system is less than 1 K, which is much smaller than the exchange interaction. The almost-gapless spin-liquid state is possibly realized in this system.

Acknowledgment

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