Magnetic order and charge separation in 2D distorted triangular lattice systems $\beta'$-X[Pd(dmit)$_2$]$_2$

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Abstract

Magnetic properties of organic compounds with two-dimensional distorted triangular lattice structure, $\beta'$-X[Pd(dmit)$_2$]$_2$ are investigated by the muon spin relaxation ($\mu$SR) method, where X is counter cation. We have previously reported that the X = Me$_4$P salt (1, Me = CH$_3$) shows a very sharp antiferromagnetic (AFM) transition at 39.3 K. We have carried out $\mu$SR measurements on other two Pd(dmit)$_2$ salts: the X = Et$_2$Me$_2$P salt (2, Et = C$_2$H$_5$) and the Et$_2$Me$_2$Sb salt (3). In compound 2, an AFM transition at lower $T_N = 15$ K with a smaller enhancement of the muon spin relaxation is observed, indicating a larger effect of the spin frustration than in 1. The zero-field $\mu$SR time spectra of 3 showed an enhancement of the relaxation below $\sim$80 K, but did not show precessions. Recently, it has been suggested that this salt undergoes a phase transition to a charge-separated nonmagnetic state. It is expected that the enhancement of the relaxation is related to the spin localization attributable to the charge separation.

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1. Introduction

Magnetic properties of the spin-frustrated antiferromagnet on an $S = \frac{1}{2}$ two-dimensional (2D) triangular lattice have been a subject of active research. The effects of the spin frustration in 2D organic conductors with an approximately triangular lattice structure have been pointed out from a theoretical point of view [1]. On the other hand, experimental reports for such systems, particularly as regards the finite-temperature behavior, are still quite few [2,3].

$\beta'$-X[Pd(dmit)$_2$]$_2$ (dmit = 1,3-dithiol-2-thione-4,5-dithiolate, C$_3$S$_5$) has a 2D distorted triangular lattice structure of the Pd(dmit)$_2$ dimers, where X is the counter cation. The deviation from the regular triangular lattice structure differs with modification of the cation, and the salts exhibit such various physical properties as superconductivity and long-range magnetic ordering, depending on this spatial anisotropy or the application of pressure [1]. In the insulating phase, a spin-$\frac{1}{2}$ is localized on each dimer with interdimer antiferromagnetic (AFM) interactions. It has been pointed out that the deviation from the regular triangular lattice structure within the layer is the most significant factor to lead to the long-range ordering, unlike other quasi-2D systems, where the transition temperature may be related to the interlayer couplings [4,5]. We have reported that one of the compounds, X = Me$_4$P salt (1, Me = CH$_3$), exhibits the AFM ordering with a very sharp transition at $T_N = 39.3$ K [6]. We have also suggested there that the time scale of the muon spin relaxation ($\mu$SR) measurement is useful to detect the spin dynamics associated with the dimensional crossover from 2D to 3D in these peculiar magnetic systems. Therefore, we carried out the $\mu$SR measurements on two other Pd(dmit)$_2$ salts, the Et$_2$Me$_2$P salt (2, Et = C$_2$H$_5$) and the Et$_2$Me$_2$Sb salt (3),
to investigate their magnetic properties. The in-plane structures of the salts 1-3 are different in the spatial anisotropy: the triangular lattice in 1 is the most anisotropic, while that in 3 is the most isotropic (namely the most spin-frustrated). The anisotropy in 2 is the intermediate.

Here we report the magnetic states of 2 and 3 observed by the μSR measurements. In the zero-field (ZF)-μSR measurement on 2, the long-range AFM ordering is observed below 15 K. The muon spin relaxation rate diverged more slowly in 2 than in 1, just above $T_N$. The ZF-μSR time spectra of 3 show an enhancement of the muon spin relaxation below ~80 K, but did not show precession. The relaxation continued to be fast down to 1.5 K.

2. Experimental

Polycrystalline samples of 2 and 3 were prepared by the air oxidation of a solution. The sample, packed into a silver foil to be plate-shaped with ~1 mm thickness, was fixed onto the sample holder of a 4He cryostat. The experiments were carried out at Port-2 in the RIKEN-RAL Muon Facility. The muon with the initial spin direction parallel to the momentum was injected into the sample.

3. Results and discussion

Fig. 1 shows the ZF-μSR time spectra of 2. Muon spin precession signals are clearly observed below 15 K, indicating the appearance of the long-range AFM ordering. The transition temperature $T_N$ is almost consistent with $^{13}$C NMR result [7]. The time spectra above $T_N$ are fitted by using the following relaxation function:

$$A(t) = Ae^{-\langle \lambda \rangle^2} e^{-\lambda t},$$  \hspace{1cm} (1)

where $\lambda$ is the distribution width of the internal field due to the nuclear dipoles (temperature-independent), and $\lambda$ is the muon spin relaxation rate to describe dynamical fluctuations. Background is already subtracted. Below $T_N$, the time spectra are fitted by a relaxation function containing two oscillation components. A 1/4 tail is not observed here even at the lowest temperature because of a finite longitudinal relaxation time.

The temperature dependences of the muon spin relaxation rate, $\lambda$, and the internal fields corresponding to the precession frequencies are shown in Figs. 2(a) and (b), respectively. $\lambda$ is fitted by $\lambda(T) = C(T - T_N)^{-\nu} + \lambda_0$, where $C$ and $\lambda_0$ are constants. Under the assumption that $\lambda \propto \xi$, where $\xi$ is the magnetic correlation length, $T_N = 14.8(3)$ K is obtained for the mean-field value ($\nu = 0.5$) for Heisenberg antiferromagnets. The fitting result is shown with a solid curve in Fig. 2(a). The muon spin precession signals suddenly appear at around $T_N$ with finite values (Fig. 2(b)). It is noted that...
the critical behavior observed in the μSR measurement is different from that in the NMR one because of the different time window. The NMR measurement continuously observes critical slowing down deriving from two kinds of crossover in this salt: the “frustration-release” crossover, which is the crossover from the frustrated paramagnet on the approximately triangular lattice to a 2D antiferromagnetically correlating state due to small deviation from the regular triangle, occurring at higher temperatures and the dimensional crossover from 2D to 3D just above $T_N$. We have suggested that the μSR measurement just emphasizes the dimensional crossover, which arises from enough growth of the correlation length within the layer, $\xi$ [6,8]. It has been suggested that $\xi$ rapidly grows in more anisotropic system [5]. Therefore, the slower enhancement of the relaxation in 2 indicates the larger spin frustration than in 1. It is also expected that the lower $T_N$ is affected the frustration, because the enough growth of $\xi$ is significant for the appearance of the long-range ordering, not the interlayer couplings, in these salts [4,5].

In contrast to the compound 2, no long-range ordering is observed in 3. Fig. 3 shows the ZF-μSR time spectra of 3. The muon spin relaxation becomes fast below ~80 K. Recently it has been found by the resistivity, X-ray structure and magnetic measurements, this salt undergoes a first-order phase transition to a charge-separated nonmagnetic state at $T_{CS}$~70 K [9,10]. The temperature where the muon spin relaxation starts to be fast is almost consistent with $T_{CS}$. The time spectra are fitted by using Eq. (1). This salt is metallic above $T_{CS}$, while it is expected that two electron spins are localized on every other dimer forming the singlet state below $T_{CS}$ [11]. Probing the internal field microscopically, the situation is similar to some nonmagnetic systems such as the spin-Peierls (SP) one. Indeed, similar ZF-μSR time spectra have been reported in an organic SP system, MEM(TCNQ)$_2$ [12,13].

Fig. 4 shows the temperature dependences of $\lambda$ and $\Delta$. $\lambda$ starts to increase at around 80 K with decreasing temperature, and is eventually saturated. Above ~120 K, $\Delta$ decreases with increasing temperature due to a motional narrowing effect. As temperature decreases from 120 K, $\Delta$ is temperature-independent down to ~50 K, and then starts to drop. Quite similar behavior in $\lambda$ and $\Delta$ is observed in the organic SP system [12], in which the magnetic gap opens in the magnetic excitation spectrum at the transition temperature and widens with decreasing temperature.

The increase in $\lambda$ below 80 K implies that the correlation time of the electronic spin fluctuations continue to be slow enough to be detectable with the μSR time scale. It is expected that the thermally activated excitations across the gap is ascribed to the muon spin relaxation, as well as in the SP systems. The shapes of the time spectra gradually change from Gaussian-type to exponential, in the temperature range from 40 to 20 K. In this range, the temperature dependence of $\lambda$ for the longitudinal-field (LF) μSR measurement show a broad maximum (not shown here). Therefore, the relaxation mechanism below

![Fig. 3. ZF-μSR time spectra of the Et$_2$Me$_2$Sb salt (3). The solid lines indicate the best fits to Eq. (1).](image1)

![Fig. 4. Temperature dependences of (a) the relaxation rate $\lambda$ and (b) the field distribution width $\Delta$ in the Et$_2$Me$_2$Sb salt (3).](image2)
~20 K is expected to be different from that in the higher temperature region. We expect that dilute defect spins, existing naturally or yielded by implantation of the muon, cause the temperature-independent relaxation below 20 K.

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