Antiferromagnetic Ordering in Quasi-Triangular Localized Spin System, \( \beta' \)-Et\(_2\)Me\(_2\)P[\( \text{Pd(dmit)\(_2\)} \)\(_2\), Studied by \(^{13}\)C NMR

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(Received January 30, 2014; accepted March 4, 2014; published online April 17, 2014)

We performed \(^{13}\)C NMR measurements of a selectively \(^{13}\)C isotope-labeled single-crystal sample of a frustrated spin system, \( \beta' \)-Et\(_2\)Me\(_2\)P[\( \text{Pd(dmit)\(_2\)} \)\(_2\). A long-range antiferromagnetic (AF) ordering below 17 K was confirmed by the observation of NMR spectrum broadening and well split resonance lines at lower temperatures. NMR spectra in the AF state can be well explained by a two sublattice model. From the analysis of the angular dependence of the NMR spectrum, we clarified the magnetic structure in the AF state, where the easy and hard axes are the crystallographic c*- and b-axes, respectively, and the effective localized moments are quite small, \( \sim 0.28 \mu_B \)/dimer. This suggests a strong quantum fluctuation effect due to magnetic frustrations in a quasi-triangular spin-1/2 system.

1. Introduction

\( \beta' \)-X[\( \text{Pd(dmit)\(_2\)} \)\(_2\) (\( X = \text{Me}_4\)P, Et\(_2\)Me\(_2\)P\(^+\), etc. and dmit = 1,3-dithiol-2-thione-4,5-dithiolate) are known as two-dimensional (2D) Mott insulators in which a spin-1/2 localizes on each \( \text{Pd(dmit)\(_2\)} \) dimer. Quarter-filled electronic bands are expected in “2 : 1” charge transfer salts with a monovalent cation. When there is a strong dimerization, however, the electronic band becomes half-filled. In fact, the calculated intradimer transfers in the present \( \text{Pd(dmit)\(_2\)} \) system are found to be much larger than the interdimer ones.\(^1\),\(^2\) From an experimental point of view, most \( \text{Pd(dmit)\(_2\)} \) compounds are insulators at ambient pressure, so that these systems are considered as Mott–Hubbard insulators. In some salts in this family, long range antiferromagnetic (AF) orderings with a large variety of transition temperatures, \( T_N \), have been confirmed.\(^3\) A series of \( \beta' \) type cation salts based on \( \text{Pd(dmit)\(_2\)} \) were systematically investigated by structural and transport measurements by Kato and coworkers.\(^1\),\(^2\),\(^4\),\(^5\) In this family of compounds, dimers of organic molecules \( \text{[Pd(dmit)\(_2\)]\(_2\)} \) form a two-dimensional quasi-triangular lattice as shown in Fig. 1(b). The authors found a close correlation between the anisotropy of the triangle and \( T_N \). For example, the \( \text{Me}_4\)P salt, which has the largest anisotropy among the compounds thus far investigated, shows AF ordering at a very high temperature of 42 K, while the Et\(_2\)Me\(_2\)P salt with a smaller anisotropy does only below 17 K.\(^3\) It is thus quite reasonable to expect that the anisotropy of the triangle reduces frustrations, which lead to a higher \( T_N \). Actually, the EtMe\(_3\)Sb salt, which has a much smaller anisotropy than these two salts, shows no sign of magnetic ordering down to the lowest temperature and the possibility of a quantum spin liquid state is discussed.\(^6\) The salt with the most symmetric triangular lattice in this family, Et\(_2\)Me\(_2\)Sb salt, was found to have a nonmagnetic spin-singlet ground state with charge separation.\(^7\)

A specific characteristic of this family of compounds is that the conduction band is based on the highest occupied molecular orbital (HOMO) of the \( \text{Pd(dmit)\(_2\)} \) molecule, instead of on the lowest unoccupied molecular orbital (LUMO) as is expected in an acceptor-based conductor. This is because of special situations in the present system, that is, a narrow energy gap between the HOMO and LUMO of the \( \text{Pd(dmit)\(_2\)} \) monomer and their strong nature of dimerization. These lead to the inversion of the antibonding HOMO and bonding LUMO bands, and as a result the antibonding HOMO band carries the conduction. A strong two-dimensional nature is believed to be characteristic of the HOMO band. The narrow gap between HOMO and LUMO also causes a strong hybridization of the HOMO of one molecule and the LUMO of the countermolecule within a dimer, which results in an appreciable charge polarization within a \( \text{[Pd(dmit)\(_2\)]\(_2\)} \) dimer, as revealed by a recent theoretical study.\(^8\)
μSR, $^1$H/$^{13}$C NMR, and ESR studies were carried out to study the AF ordering state of the title material, Et$_2$Me$_2$P salt. An abrupt enhancement of the μSR relaxation rate and NMR linewidths and the observation of antiferromagnetic resonance (AFMR) have evidenced long-range AF ordering at ~17 K. Since the μSR measurements were carried out for a polycrystalline sample, however, no information on the magnetic structure of the AF ordering was obtained. Our previous $^1$H NMR and $^{13}$C NMR studies of a fully $^{13}$C-labeled sample could not approach the AF state either, because the observed spectrum in this sample was just broadened without any structure. Only an AFMR study has suggested the direction of the AF moment that the easy axis is the c-axis. Therefore, any other detailed information on the magnetic structure including the magnitude of localized AF moment has not been clarified yet.

In the present study, we used selectively $^{13}$C labeled single-crystal sample in order to reduce the number of NMR active nuclear sites probing the magnetic structure. The $^{13}$C-labeled sites are shown in Fig. 1(a). The reduction in the number of probe nuclear sites was found to be quite advantageous in analyzing the spectrum, since well-separated peaks were observed in the AF state in contrast to the broadened spectrum observed previously in the fully $^{13}$C-labeled sample.

2. Experimental Procedure

Selectively $^{13}$C-isotope (spin $I = 1/2$)-labeled ligands, dmit, were synthesized by the method described elsewhere. Single crystals of β-Et$_2$Me$_2$P[Pd(dmit)$_2$]$_2$ salt were prepared by the air oxidation of (Et$_2$Me$_2$P)$_2$[Pd(dmit)$_2$] in acetone containing acetic acid. NMR measurements were performed with a phase-coherent pulsed NMR spectrometer. An NMR spectrum was obtained by the fast Fourier transformation (FFT) of spin echo signals made by a π/2–π pulse sequence at a fixed magnetic field. The external field $H_0$ was provided by a superconducting magnet. We used two different values of the external field, $H_0 = 7.0$ and 8.3 T, which were calibrated by a $^{63}$Cu signal from the resonance coil, but experimental results were essentially the same. The typical linewidth in the paramagnetic state was a few kHz, which was narrow enough to observe the entire spectrum with a single rf pulse. In contrast, the line shift due to the long-range magnetic ordering in the AF state was much larger than the rf pulse strength. To cover the entire spectrum with such large peak shifts, we applied the so-called frequency step and sum (FSS) method. We changed the reference frequency with a step of 50–100 kHz, detected the FFT spectrum at every step and accumulated them.

First, we measured the temperature dependence of the NMR spectrum with a field applied perpendicular to the $ab$ plane. We confirmed the transition from a paramagnetic state to an AF state. Then we measured the angular dependence of the NMR spectrum in the AF state by rotating the external field in the $ac^*$ and $bc^*$ planes.

3. Results and Discussion

3.1 Temperature dependence of NMR spectrum

The $^{13}$C NMR spectrum in the external field perpendicular to the 2D plane was measured down to 1.8 K. The external field was 8.3 T for most of the spectra, except that at 1.8 K, which was taken at a field of 7.0 T under careful consideration to avoid possible saturation due to an unexpected long relaxation time. We confirmed that the observed spectrum was essentially the same as that previously obtained.

The temperature dependence of the linewidth determined as the square root of the second moment of the observed spectra is shown in Fig. 2. The inset shows typical NMR spectra at several temperatures. Here, the horizontal axis is the frequency measured from $yH_0$, where $y$ and $H_0$ are the gyromagnetic ratio of the $^{13}$C nucleus and the externals field, respectively. The linewidth at high temperatures is smaller than that observed in our previous study on a fully $^{13}$C-labeled sample. This is clearly because the number of NMR-active nuclear sites in the present sample was reduced and thus the inhomogeneous broadening caused by the site dependence of the local fields was remarkably reduced. An abrupt broadening of the linewidth occurs below the reported Néel temperature, $T_N \sim 17$ K, and four well-separated peaks due to the AF long-range ordering (LRO) appear at lower temperatures. The four peaks in the AF state suggest that there are four independent $^{13}$C sites in this geometry ($H_0 \perp ab$ plane). This is explained by the collinear structure of magnetic ordering, which has two sublattices, rather than the 120 deg structure expected in a strongly frustrated triangular system. We expect eight peaks at maximum because there are two nonequivalent $^{13}$C sites in a 2D layer, and two kinds of layer (layer1/layer2) and two kinds of AF moment (up/down) exist. The difference between layer1 and layer2 is in the stacking direction of dimers, which is the $a + b$ or $a - b$ axis, respectively. Layer1 and layer2 are crystallographically equivalent, but they become nonequivalent when the external magnetic field is applied in a general direction. In this geometry ($H_0 \perp ab$ plane), however, they are equivalent and four peaks should appear. In fact, when the magnetic field is tilted from this direction, the number of peaks increases, as shown in the following subsection; we can distinguish peaks from different layers.

3.2 Asymmetry of electron distribution within a molecule

Next, we pay attention to the separation of the two peaks on each side of the spectrum. It should be explained by the
difference in the environment at the $^{13}$C sites on both sides of the Pd(dmit)$_2$ molecule. The $\pi$ orbitals of $^{13}$C sites on both sides tilt slightly with each other because of the molecular bonding due to the strong dimerization. It is found, however, that this effect is too small to explain the observed peak separation. Another possible reason for this difference is the asymmetry of electron (spin) density within a molecule. The large peak separation in the observed spectrum seems to indicate that the microscopic environments on both sides of a molecule are magnetically different.

Electron distributions in a pure HOMO for an isolated Pd(dmit)$_2$ monomer are expected to be symmetric within a molecule. When two molecules form a dimer, however, some charge disproportionation within a molecule may appear. This is because the HOMO of the Pd(dmit)$_2$ monomer hybridizes with the LUMO of the other monomer within a dimer, since the HOMO–LUMO gap of the Pd(dmit)$_2$ monomer is relatively small and the symmetry with respect to the left and right dmit ligands is broken upon dimer formation. A recent first-principles calculation study\(^9\) has revealed an appreciable asymmetry of the electron distribution within a molecule. The band at the Fermi level comes from the antibonding pairs of HOMOs of a Pd(dmit)$_2$ molecule forming the dimer. However, there exists a band based on the bonding LUMOs nearby. The asymmetry of the charge distribution derived by the first-principles calculation could be attributed to the hybridization with the bonding LUMO band.

Table I shows the list of electron distributions in HOMO at several dominant sites calculated for a monomer, Pd(dmit)$_2$, by extended Hückel MO calculation with Mulliken population analysis using the crystallographic structural data at room temperature. The values were divided by 2, in order to normalize them to one per Pd(dmit)$_2$ dimer, for use in later analyses. The electron distributions in HOMO already exhibit an appreciable asymmetry, which comes from geometrical asymmetry of the molecule since atomic coordinates determined crystallographically in solid were used.

The observed $^{13}$C NMR spectrum claims that the asymmetry of the charge density in the Pd(dmit)$_2$ molecule is larger than that expected from the extended Hückel MO calculations. We write the electron distributions at the left and right atomic sites as $\delta(1 \pm \eta)$, by introducing the adjustable parameter $\eta$ to represent the asymmetry of the electron distribution between them. The values given in Table I are written as 0.0096(1 ± 0.09) for C5 and C6, and as 0.0772(1 ± 0.06) for S9 and S10. As will be discussed later, the asymmetry parameter $\eta$ is estimated to be $\eta \sim -0.25$, to reproduce the observed $^{13}$C NMR spectrum. The sign of $\eta$ should be negative, which means that the C6 site carries a higher electron density than C5. This conflicts with the above results by the extended Hückel MO calculations. In contrast, the first-principles calculation based on density-functional theory (DFT) within the generalized gradient approximation (GGA)\(^{16}\) proposed an estimate of $\eta \sim -0.12$, which is in agreement with the observation, at least, qualitatively. Unfortunately, a direct estimate of the absolute value of the electron distribution at each atomic site is not an easy task for the first-principles DFT calculation.

To confirm the large electron asymmetry within a molecule, we measured the spin lattice relaxation rate $T_1^{-1}$ around 2.0 K for the different peaks shown in the inset of Fig. 2. Since the observed nuclear relaxation curves were not single-exponential, we used a stretched exponential decay given as $\sim \exp[-(\tau/T_1)^b]$. Non-single-exponential relaxations were often observed in magnetically ordered states, suggesting an intrinsic inhomogeneity in local field fluctuations. We found that $T_1^{-1}$ and $\beta$ are 0.018 ± 0.0005 s$^{-1}$ and 0.66 for the peak with a smaller frequency shift and 0.055 ± 0.002 s$^{-1}$ and 0.62 for that with a larger frequency shift, respectively; the ratio of $T_1^{-1}$ is 1.0 : 3.0. Assuming that the spin and charge densities are proportional with each other and that AF fluctuations at both the sites are the same, we expect that $T_1^{-1} \propto \delta^2 \propto (1 \pm \eta)^2$; the ratio of $T_1^{-1}$ should be 0.75 : 1.25 $\approx$ 1.0 : 2.78, which is in good agreement with the observed ratio.

### 3.3 Angular dependences of NMR spectrum and magnetic structure in the AF state

The angular dependence of the NMR spectrum in the AF state is shown in Fig. 3. The angle of external field was measured from the $c^*$-axis, the normal axis of the molecular layer, as shown in the insets. Peak positions are plotted against the field orientation in Fig. 4. The solid lines exhibit the results of the simulation to be described later. In the $ac^*$ rotation, there are four observed peaks, corresponding to independent $^{13}$C sites, since layer1 and layer2 are equivalent in this geometry. Furthermore, the angular dependence as a whole seems to suggest a 90° periodicity. On the other hand, in the $bc^*$ rotation, more peaks (at most eight) are distinguished. We also notice discontinuous changes in the peak positions around $\phi \approx \pm 60°$.

These characteristic behaviors of the NMR spectrum should contain important information of the magnetic structure of the AF state. We calculated the peak positions with reasonable assumptions on possible magnetic structures and tried to reproduce the observed angular dependence. We used the crystallographic structural data at room temperature.\(^3\) Assumptions in the present simulation are listed as follows.

1) Magnetic dipole fields $H_{\text{dip}}$ at the site of the $^{13}$C nuclear spin $i$ made by the localized moments distributed in the surroundings are taken into account. The off-site contribution of the magnetic moments $\mu_j$ at neighboring atomic sites $j$ is given easily by a well-known formula for dipolar fields. Considering that only the component parallel to the external field is responsible for the resonance shift, $\Delta \omega_i$, we obtain

$$\Delta \omega_i^{\text{off}} \approx \sum_{j \neq i} \gamma H_{\text{dip}} \cdot \hat{H}_0$$

$$= \sum_{j \neq i} \gamma \frac{\mu_j}{r_{ij}^3} [(3 \hat{r}_{ij} \cdot \hat{r}_{ij})(\hat{r}_{ij} \cdot \hat{H}_0) - (\hat{r}_{ij} \cdot \hat{H}_0)],$$

where $r_{ij}$ is a position vector joining a point dipole $\mu_j$ and the $^{13}$C site $i$. Hat symbols denote unit vectors parallel to corresponding vectors.
2) The localized magnetic moment per Pd(dmit)$_2$ dimer is denoted as $\sigma_{i}^{\mu_B}$, where $\mu_B$ is the Bohr magneton and $\sigma$ is a fitting parameter for describing a possible reduction in the localized moment due to spin fluctuations. Furthermore, the magnetic moment is distributed on each atomic site within a [Pd(dmit)$_2$]$^2$ dimer with a spin density $\delta_j$. The values $\delta_j$ are normalized to one per dimer. Taking $\mu_j = \mu_B \delta_j \sigma$, the off-site contribution for the resonance shift is given as

$$\Delta \omega_i^{\text{off}} = \sum_{j \neq i} \frac{\sigma \mu_B \delta_j}{r_{ij}^3} \left[ (3 \hat{\mu}_j \cdot \hat{r}_{ij})(\hat{r}_{ij} \cdot \hat{H}_0) - (\hat{\mu}_j \cdot \hat{H}_0) \right]. \tag{3}$$

3) The dominant contribution of the dipolar fields at $^{13}$C site $i$ comes from the on-site $\pi$-electron, for which the term $1/r^3$ should be averaged for the $\pi(2p_\pi)$-orbital

$$\Delta \omega_i^{\text{on}} = \gamma (\sigma \mu_B \delta_j) \frac{2}{5} \left[ \frac{1}{r^3} \right] (3 \hat{\mu}_j \cdot \hat{r}_{ij})(\hat{r}_{ij} \cdot \hat{H}_0) - (\hat{\mu}_j \cdot \hat{H}_0), \tag{4}$$

where $\delta_j$, $1/r^3$, and $\hat{r}_{ij}$ are the spin fraction on the considered site $i$, the average $1/r^3$ for the $2p_\pi$ orbital, and the unit vector along the $2p_\pi$ orbital, respectively. The factor $2/5$ comes from the angular integral for the $2p_\pi$ orbital.

4) Since the external field of the present measurement is much larger than the spin flop field of $\approx 1.0$ T, the localized moments are expected to be always perpendicular to the field. Thus, the last terms of Eqs. (3) and (4) can be neglected and the resonance shifts are given as

$$\Delta \omega_i = \Delta \omega_i^{\text{on}} + \Delta \omega_i^{\text{off}} = \gamma (\sigma \mu_B \frac{2}{5} \left[ \frac{1}{r^3} \right]) \delta_j (3 \hat{\mu}_j \cdot \hat{r}_{ij})(\hat{r}_{ij} \cdot \hat{H}_0)$$

$$+ \sum_{j \neq i} \frac{1}{r_{ij}^3} \delta_j (3 \hat{\mu}_j \cdot \hat{r}_{ij})(\hat{r}_{ij} \cdot \hat{H}_0), \tag{6}$$

5) The direction of the AF moments $\hat{\mu}_j$ depends on the direction of the external field with respect to the principal axes of the magnetic anisotropy; the easy, intermediate, and hard axes. We considered three ideal cases: Case A is the case in which the magnetic field is rotated in a plane perpendicular to the easy axis, where the AF moments stay parallel to the easy axis; the periodicity of the angular dependence of resonance shift should be $180^\circ$. Case B is the case in which the magnetic field is rotated in a plane perpendicular to the hard axis, where the AF moments stay in the plane and rotate together with the field maintaining its...
direction perpendicular to the field; the periodicity of the angular dependence of resonance shift should be 90°. Case C is the case in which the magnetic field is rotated in the plane perpendicular to the intermediate axis, where the situation is a little more complicated than those in the previous two cases; while the moments stay in the plane, as in Case B, as long as the field direction is not far from the hard axis, when the field approaches the easy axis, the moment flips up to the perpendicular direction, as in Case A, to avoid approaching the hard axis.

3.4 Simulation of angular dependence of resonance shifts using calculated electron densities

The observed angular dependence in the ac* rotation clearly suggests a periodicity of 90°, indicating that Case B should be applied in this rotation; the b-axis is the magnetic hard axis. In the bc* rotation, actually, spin-flop phenomena are observed around φ ≃ ±60°, as expected in Case C; the c* - and a-axes are the easy and intermediate axes, respectively. It is consistent with the the results of the AFMR measurement, which claim that the easy axis is the c-axis.

Since the resonance shifts all contain a single parameter, σ, with which the whole spectrum is scaled, we first tried to reproduce the angular dependence of the relative positions of peaks from independent 13C sites and then adjust σ to fit the calculated spectra to the observed ones. We take the average 1/ρ2 for the on-site 2p orbital as 1.35 × 1023 cm−3. As for the electron distribution δi on each atomic site, we applied the values calculated by the extended Hückel molecular orbital method given in Table I. The on-site electron distributions δi were taken to be 0.0096(1 ± η) for C5 (–) and C6 (+) sites using the asymmetry parameter η as another fitting parameter. The best fit was obtained with η ~ 0.25, instead of the values of η ~ 0.09 calculated by the extended Hückel MO calculation or η ~ −0.12 calculated by the first-principles DFT. Small but non-zero off-site contributions were dominated by the sulfur sites (S9 and S10) at both ends of a molecule, and all the other contributions were negligible. We calculated the off-site contributions by assuming that the charge distributions at the sulfur sites also reflect the asymmetry given by the same η as that for the on-site contributions.

The last parameter is σ representing a possible reduction in localized AF moment. We found that the observed peak positions were well reproduced by σ ~ 0.28 and 0.25, for the ac* and bc* rotations, respectively, which suggests a large reduction in the localized AF moments. These values are in good agreement with each other, considering that only two parameters, i.e., σ and η, were used for the simulation. The discrepancy between the values of σ for the different field rotations probably comes from the oversimplified estimates of the off-site contribution using point dipole approximations and/or the improper choice of electron distribution parameters, δi.

3.5 Estimate of σ using anisotropic component of hyperfine coupling constant

The estimates of σ described above depend on the calculated values of electron/spin distributions. We wanted to find another method of estimating σ from purely experimental points of view. The 13C NMR spectrum in the AF state is determined by the hyperfine coupling between the AF localized spins and 13C nuclear spins. The angular dependence of peak positions should reflect the anisotropic component of the hyperfine coupling. We estimated the value of the anisotropic component of the hyperfine coupling constant Aaniso from our study of a polycrystalline sample of the β-Et2Me2Sb salt, another member of the β-Pd(dmit)2 family. In this salt, the ground state is not AF, but a nonmagnetic spin-singlet state (charge-separated state) below 70 K.

The observed spectrum of the β-Et2Me2Sb salt shows typical powder patterns with a uniaxial symmetry both above and below the transition, as shown in the inset of Fig. 5. In this salt, it was revealed that neutral and divalent dimers coexist below the transition because of charge separation. However, the line shape shows a usual powder pattern with a uniaxial symmetry, apart from a small structure around the central region. This fact suggests that the chemical shift tensor does not change so much between the neutral and divalent dimers. It also seems reasonable to assume that the chemical shift is independent of temperature. Note that the principal value parallel to the symmetry axis, D1., is smaller than that perpendicular to the axis, D1., that is, the anisotropic component is negative.

At higher temperatures, the linewidth is much smaller than that below the transition. In this region, a finite spin susceptibility and thus Knight shift should recover. The observed spectrum still shows a typical powder pattern with a uniaxial symmetry. This clearly indicate that the hyperfine coupling also shows a uniaxial symmetry and the principal axes correspond to those of the chemical shift tensor. The reduction in the linewidth should be due to the partial compensation of the chemical shift tensor with the Knight shift (hyperfine) tensor, since the anisotropic hyperfine coupling constant Aaniso for π-electrons is positive.

The linewidth, determined as the square root of the second moment of the observed spectrum, is plotted against susceptibility in Fig. 5. The straight line shows the relation (linewidth)/γH0 = −262ϕdimers/μB + 6.11 × 10−5. The negative slope is due to the opposite sign between the chemical and Knight shift tensors. Using the relation Kani = √5/4(linewidth)/γH0 for a uniaxial symmetry, we obtain Aaniso ~ 293 Oe/μB.
To apply the above hyperfine coupling constant to the present simulation, we assumed a uniaxial hyperfine coupling with the principal axis parallel to the 2p, orbital of $^{13}$C, $\vec{r}_0$, considering that the observed spectrum of the Et$_4$Me$_2$Sb salt was well explained with this assumption. Using the parameter $\eta$ for the asymmetry in the spin/charge distribution in a molecule as before, we obtained the resonance shifts as follows:

\[ \Delta \omega_i = \gamma A_{\text{aniso}} \mu_B \sigma (1 \pm \eta) \left( \langle \vec{\mu}_i \cdot \vec{r}_0 \rangle \langle \vec{r}_0 \cdot \vec{H}_0 \rangle \right) . \]  

(7)

Note that one would obtain the usual expression for the anisotropic component of the Knight shift, by replacing the factor $\mu_B \sigma$ by $\chi_{\text{molecule}} H_0$ ($\chi_{\text{molecule}}$ is the spin susceptibility per molecule, or dimer, as in the present system), taking $\vec{\mu}_i = \vec{H}_0$ in a paramagnetic state and restoring the last term of Eq. (3) or (4) as $-\vec{\mu}_i \cdot \vec{H}_0 = -1$. Here, $A_{\text{aniso}}$ should contain the on-site dipolar field as the main contribution and all other off-site contributions on average. The angular dependence of the peak positions was calculated using this formula and $A_{\text{aniso}} \mu_B \approx 293$ Oe. The best fit was obtained with the parameters $\sigma \approx 0.28$ and $\eta \approx -0.25$, which are shown by solid lines in Fig. 4. Note that the single parameter $\sigma$ could explain all the results for both rotations consistently. This estimate of $\sigma$ on a purely experimental basis is very close to those derived from the electron distributions given by the extended Hückel MO calculation, after taking into account a proper asymmetry in electron distributions within a molecule. An appreciable reduction in the localized moment per Pd(dmit)$_2$ dimer, $\sigma \approx 0.28$, was confirmed.

4. Conclusions

We performed $^{13}$C NMR measurements using a selectively labeled single-crystal sample of $\beta$-Et$_4$Me$_2$P[Pd(dmit)$_2$]$_2$ at ambient pressure. Three-dimensional AF ordering was confirmed by observing an abrupt broadening of the NMR spectrum below the reported Néel temperature, $T_N \approx 17$ K. Well split peaks appeared at lower temperatures in the AF state and the angular dependence of the peak positions could be explained by a two-sublattice model. The principal axes of the AF anisotropy were determined; the easy and hard axes are the crystallographic $c^*$- and $b$-axes, respectively. It was confirmed that the localized magnetic moment at low temperatures in the AF state was remarkably reduced as 0.28 $\mu_B$ per Pd(dmit)$_2$ dimer.

Large quantum spin fluctuations are generally expected in AF spin-1/2 systems. In a two-dimensional triangular lattice, a strong magnetic frustration should enhance the spin fluctuations, which might lead to a quantum disordered phase, a spin-liquid state. In a symmetric triangular lattice, however, many theoretical studies have predicted that the ground state will be neither a spin liquid state nor a Néel (collinear) LRO state but a spiral LRO state with a 120 deg structure. Various theoretical calculations for the reduction in the staggered moment have been published; the linear spin-wave theory, for example, predicts $\langle S_z \rangle \approx 0.239$ for the spiral LRO ground state, which corresponds to our reduction parameter $\sigma \approx g \langle S_z \rangle \approx 0.48$ with the electronic g-factor $g = 2$. Our experimental estimate of $\sigma \approx 0.28$, given above, is much smaller than any theoretical estimates thus far obtained.

Recently, the effects of asymmetry in quasi-triangular lattices have been systematically investigated with a modified spin-wave theory as well as by an exact diagonalization method and the existence of a magnetically disordered state at the boundary between the LRO’s Néel and spiral states has been predicted. The state of the present material, the Et$_4$Me$_2$P salt, may be very close to that at the boundary with the quantum disordered state. To confirm this picture, it is very crucial to investigate the Me$_4$P salt with a higher $T_N$ to compare its results with the present results for the Et$_4$Me$_2$P salt.

Acknowledgments

We would like to thank T. Itou (University of Tokyo), T. Tsumuraya (Riken), T. Sakurai (Kobe University), S. Ohira (J-PARC), and H. Katsura (Gakushuin University) for useful discussions. This work was supported by a Grant-in-Aid for Scientific Research on Innovative Areas (No. 20110002) from the Ministry of Education, Culture, Sports, Science and Technology and by Grant-in-Aid for Scientific Research (S) (No. 22224006) from the Japan Society for the Promotion of Science.

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