

^{13}C NMR reexamination of the valence bond solid state in $\text{EtMe}_3\text{P}[\text{Pd}(\text{dmit})_2]_2$ T. Itou^{1,*} and R. Kato²¹*Department of Applied Physics, Tokyo University of Science, Tokyo 125-8585, Japan*²*Condensed Molecular Materials Laboratory, RIKEN, Saitama 351-0198, Japan*

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Recently, the study by Miksch *et al.* [*Science* **372**, 276 (2021)] and subsequent studies have proposed that the organic system κ -(BEDT-TTF)₂Cu₂(CN)₃, which has long been regarded as a quantum spin liquid (QSL) candidate since an early nuclear magnetic resonance (NMR) report [Shimizu *et al.*, *Phys. Rev. Lett.* **91**, 107001 (2003)], actually exhibits a valence bond solid (VBS) ground state. To verify the validity and discuss the applicability of this interpretation to κ -(BEDT-TTF)₂Cu₂(CN)₃ and other potential QSL candidates, it is necessary to provide a comprehensive NMR report in a representative VBS system for comparative analysis. For this purpose, we reexamined the ^{13}C NMR study of the organic VBS system $\text{EtMe}_3\text{P}[\text{Pd}(\text{dmit})_2]_2$. We discovered that the spin-lattice relaxations in the VBS state are significantly influenced by orphan impurity spins, whose emergence is captured by the spectral results. Furthermore, we also provide the general formalism of NMR relaxations caused by the dynamics of these orphan impurity spins, which expands the Bloembergen-Purcell-Pound model. This paper will provide a robust foundation for future research discussing NMR results of QSL candidates.

DOI: [10.1103/PhysRevB.108.104410](https://doi.org/10.1103/PhysRevB.108.104410)**I. INTRODUCTION**

Quantum spin liquids (QSLs) have been one of the prominent subjects in the field of condensed matter physics. In particular, organic systems have played a significant role in the investigation of QSLs [1]. The experimental study of QSLs in organic systems has evolved from the organic compound κ -(BEDT-TTF)₂Cu₂(CN)₃. This system has been regarded as a QSL candidate for 20 years since Shimizu *et al.* reported the absence of long-range antiferromagnetic ordering [2]. Several experimental measurements have been conducted to elucidate the nature of the ground state, although these studies yield conflicting conclusions regarding either gapless or tiny-gapped nature [2–7]. A nuclear magnetic resonance (NMR) study has reported that the spin-lattice relaxation rates of this material exhibit a power-low temperature dependence down to ultralow temperatures, thus suggesting the absence of a full gap, although the relaxation curves become inhomogeneous below approximately 6 K [7]. The results of all the experimental studies were considered evidence of a fully gapless or tiny-gapped QSL.

Recently, however, an astonishing proposition has been put forth by Miksch *et al.* [8]. They conducted a meticulous electron spin resonance investigation for κ -(BEDT-TTF)₂Cu₂(CN)₃ and unveiled a rapid decrease of the intrinsic spin susceptibility at 6 K, indicating the formation of a large spin gap. They also asserted that the opening of this spin gap is highly likely attributable to the formation of a valence bond solid (VBS), in contrast to the longstanding QSL interpretation. Furthermore, Pustogow has very recently bolstered this VBS interpretation by highlighting the similarities in physical

properties exhibited by κ -(BEDT-TTF)₂Cu₂(CN)₃ and other spin-gapped systems [9].

Considering these circumstances, we firmly believe that it is imperative for experimental researchers to carefully reassess the experimental results of κ -(BEDT-TTF)₂Cu₂(CN)₃ and other QSL organic candidates to acquire correct understanding. In particular, it is crucial to reconsider the NMR results and conduct a thorough comparison between the NMR outcomes of the QSL candidates and a prototypical VBS material, as NMR has historically played a significant role in the experimental investigation of the organic QSL candidates. However, an obstacle in the process of reconsidering the NMR results arises from the lack of detailed reports elucidating the behavior of NMR quantities in prototypical organic VBS materials, despite the presence of a few fragmented reports that rather focus on transitions from the VBS state to neighboring phases [10,11].

Thus, we reexamined ^{13}C NMR study of $\text{EtMe}_3\text{P}[\text{Pd}(\text{dmit})_2]_2$ (Fig. 1) at ambient pressure, which is recognized as a representative organic VBS system [12–14]. This system is a Mott insulator at ambient pressure and undergoes a transition below 25 K into a spin-gapped nonmagnetic state accompanied by the dimerization of localized spins, namely, a VBS state. In this paper, we present ^{13}C NMR results of the inner-carbon-enriched compound. To avoid the Pake doublet structure, only one side of each inner double bond in the $\text{Pd}(\text{dmit})_2$ molecule is enriched in the inner-carbon-enriched compound, as shown in Fig. 1(d). In addition, for a comprehensive discussion, we also include previously-reported ^{13}C NMR results of the outer-carbon-enriched compound [10]. Note that the inner carbons have larger electron densities [15] and, thus, larger hyperfine couplings than the outer carbons [16].

The NMR measurements were conducted on numerous single crystals without any specific orientation for both the

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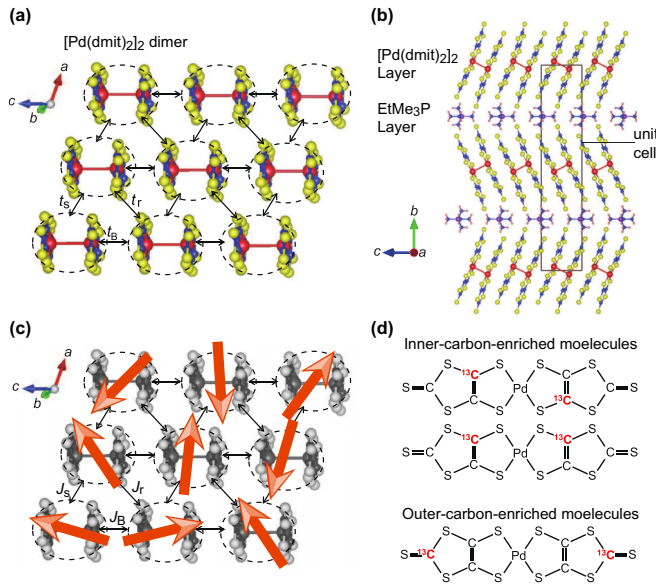


FIG. 1. (a) Top view of the crystal structure of the $[\text{Pd}(\text{dmit})_2]_2$ layer of $\text{EtMe}_3\text{P}[\text{Pd}(\text{dmit})_2]_2$. The $\text{Pd}(\text{dmit})_2$ molecules are strongly dimerized (the pairs are denoted by the dashed ovals). (b) Side view of the crystal structure of $\text{EtMe}_3\text{P}[\text{Pd}(\text{dmit})_2]_2$. Two-dimensional $[\text{Pd}(\text{dmit})_2]_2$ layers are separated by nonmagnetic layers of the closed-shell monovalent cation EtMe_3P . (c) Schematic of the spin system of $\text{EtMe}_3\text{P}[\text{Pd}(\text{dmit})_2]_2$. One electron with a $1/2$ spin is localized on each $[\text{Pd}(\text{dmit})_2]_2$ dimer. (d) ^{13}C -enriched $\text{Pd}(\text{dmit})_2$ molecules for the inner-carbon-enriched compound and the outer-carbon-enriched compound. In the inner-carbon-enriched compound, only one side of each inner double bond in the $\text{Pd}(\text{dmit})_2$ molecule is enriched, as shown in the two molecules in the upper panel, which are equally contained in the present samples.

inner-carbon-enriched and outer-carbon-enriched compounds (hereafter, these samples are referred to as the inner- ^{13}C assemblage and outer- ^{13}C assemblage, respectively.) Furthermore, we also performed ^{13}C NMR measurements on one single crystal of the inner-carbon-enriched compound (hereafter referred to as the inner- ^{13}C single crystal.) All the NMR measurements were conducted at a field of 7.65 T. In the case of the inner- ^{13}C single crystal measurement, the magnetic field was applied nearly parallel to the a^* axis within an uncertainty of $\pm 20^\circ$. Note that the hyperfine coupling components of the inner carbon sites parallel to the a^* axis (a^*-a^* components) are expected to be small and marginally negative [17].

II. RESULTS OF ^{13}C NMR SPECTRA

Figures 2(a)–2(c) show the temperature dependence of the ^{13}C NMR spectra. Because of the large hyperfine coupling of the inner carbon sites compared to the outer carbon sites [16], the spectra for the inner- ^{13}C assemblage reflect the spin susceptibility, whereas the spectra for the outer- ^{13}C assemblage are hardly affected by it. The observed spectra for the inner- ^{13}C assemblage [Fig. 2(a)] have an asymmetric structure above 25 K. This structure arises from the powder distribution of nearly uniaxial anisotropic Knight shift; Knight shift varies with the angle between the sample direction and the applied field owing to the anisotropy of the hyperfine

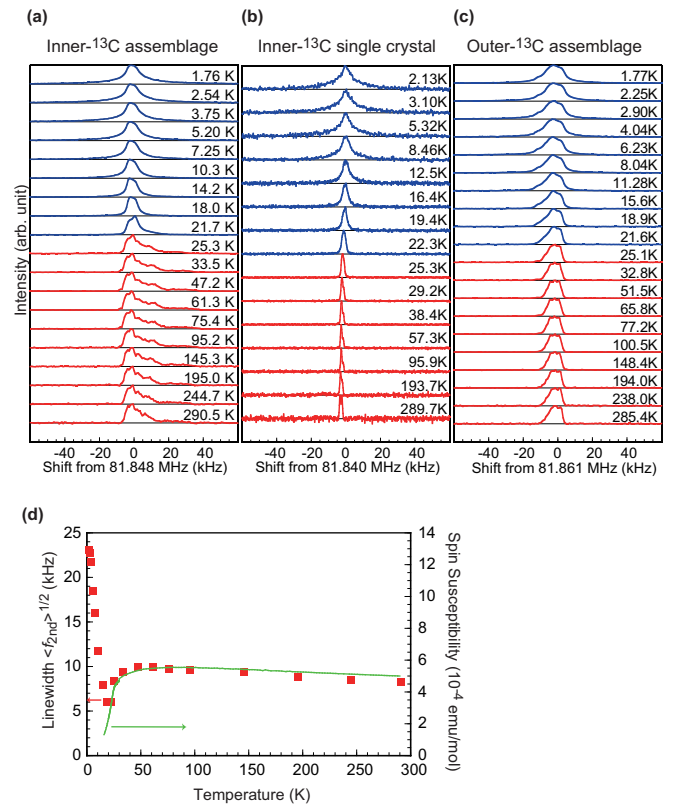


FIG. 2. (a)–(c) Temperature dependence of the ^{13}C NMR spectra of $\text{EtMe}_3\text{P}[\text{Pd}(\text{dmit})_2]_2$ for (a) the inner- ^{13}C assemblage (numerous single crystals of the inner-carbon-enriched compound without any specific orientation), (b) the inner- ^{13}C single crystal (one single crystal of the inner-carbon-enriched compound), and (c) the outer- ^{13}C assemblage (numerous single crystals of the outer-carbon-enriched compound without any specific orientation). Some of the data for the outer- ^{13}C assemblage shown in (c) has been previously reported in the early work [10]. (d) Temperature dependence of the linewidth $\langle f_{2nd} \rangle^{1/2}$ of the ^{13}C NMR spectra for the inner- ^{13}C assemblage shown in (a). The linewidth is defined as the square root of the second moment. Except for low temperatures, it accords with the temperature dependence of the spin susceptibility [12], which is displayed by the solid curve.

coupling, and the overall spectral shape is obtained as the integral of sample signals with different angles. In this case, the linewidth is expected to be proportional to the spin susceptibility. Figure 2(d) shows the temperature dependence of the linewidth $\langle f_{2nd} \rangle^{1/2}$ (defined as the square root of the second moment) of the spectra shown in Fig. 2(a). It accords with the temperature dependence of the spin susceptibility [12] in the high-temperature paramagnetic phase above 25 K. Just below 25 K, the linewidth exhibits a rapid decrease due to the rapid decrease of the spin susceptibility, as expected. However, at lower temperatures, the linewidth deviates from the behavior expected for the spin susceptibility, showing a rebroadening effect. This broadening at low temperatures is characterized by a symmetric structure, in sharp contrast to the asymmetric structure observed at high temperatures. This strongly suggests that the broadening is not caused by the powder distribution of anisotropic Knight shift but rather by

inhomogeneous broadening; that is, the internal field is not homogeneous but inhomogeneously distributed.

This result is further confirmed by the ¹³C NMR spectra obtained for the inner-¹³C single crystal [Fig. 2(b)]. The Knight shift shows a slight negative shift above 25 K because the parallel component of the hyperfine coupling in the current magnetic-field configuration ($\parallel \sim a^*$ axis) has a slight negative value. Notably, even for the spectra for the single crystal, the spectra show appreciable broadening at low temperatures in the VBS state. The broadening observed for the single crystal provides conclusive evidence for the inhomogeneous distribution of the internal field.

Because these inhomogeneous broadening structures are exclusively observed in the VBS state, it is highly probable that they are induced by orphan impurity spins located at sites where dimerization fails to occur.

III. RESULTS OF ¹³C NMR T_1^{-1}

Figure 3(a) shows the temperature dependence of the spin-lattice relaxation rate T_1^{-1} . We determined T_1^{-1} by fitting the spin-echo intensity $M(t)$ after a time delay t following saturation comb pulses to the stretched-exponential function $1-M(t)/M(\infty) = \exp\{-(t/T_1)^\beta\}$, where β [shown in Fig. 3(b)] is the stretching exponent. The intensity $M(t)$ is evaluated as the integral of the Fourier-transformed spin-echo signal over the whole frequency region of the signal. The relaxation rates T_1^{-1} of the three samples exhibit nearly identical temperature dependence at high temperatures, albeit with different absolute values. This difference arises due to the larger hyperfine couplings of the inner carbon sites than those of the outer sites [16]. Consequently, both the inner-¹³C assemblage and inner-¹³C single crystal exhibit larger T_1^{-1} values than the outer-¹³C assemblage. In addition, the inner-¹³C single crystal exhibits slightly larger T_1^{-1} values than the inner-¹³C assemblage. This observation indicates that, in the single crystal measurement under the current magnetic-field configuration ($\parallel \sim a^*$ axis), local-field fluctuations perpendicular to the applied magnetic field surpass the averaged fluctuations in all directions. This is attributed to the fact that the hyperfine coupling component parallel to the applied field ($\parallel \sim a^*$ axis) is comparatively small, as previously explained, leading to the comparatively large perpendicular ($\perp \sim a^*$ axis) hyperfine coupling components.

At high temperatures, T_1^{-1} for all the samples gradually decreases as the temperature decreases, without any notable enhancement due to critical slowing down. A drastic change is observed at 25 K, which is the VBS transition temperature. Below this temperature, T_1^{-1} exhibits a considerable decrease as expected in spin-gapped systems. This behavior is reproducible across all the three samples. According to the textbook understanding, T_1^{-1} at low temperatures for spin-gapped systems should follow an activation behavior, which is represented by the dotted curves in Fig. 3(a) using the reported gap value of ~ 40 K [12]. However, all the observed T_1^{-1} at low temperatures clearly deviates positively from the activation behaviors. This strongly indicates the appearance of an additional relaxation mechanism. Note that the extent of the deviation varies among the samples; the outer-¹³C assemblage and inner-¹³C assemblage

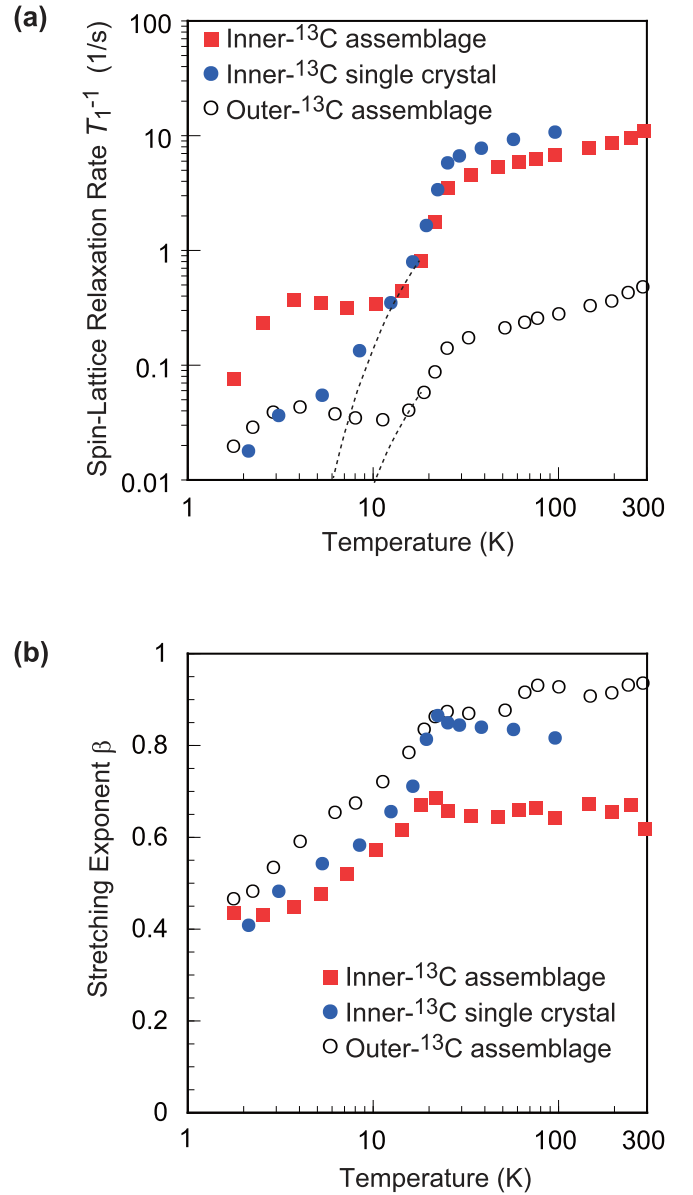


FIG. 3. (a) Temperature dependence of the spin-lattice relaxation rate T_1^{-1} of $\text{EtMe}_3\text{P}[\text{Pd}(\text{dmit})_2]_2$ for the inner-¹³C assemblage, inner-¹³C single crystal, and outer-¹³C assemblage. The dotted curves represent the expected activation behaviors based on the reported gap value of ~ 40 K [12] (b) Temperature dependence of the stretching exponent β for the three samples. [The data for the outer-¹³C assemblage in (a) and (b) are the same as those previously reported in the early work [10].]

display large deviations compared to the inner-¹³C single crystal.

To discuss the origin of the additional mechanism, it is important to analyze the temperature dependence of the stretching exponent β , which quantifies the distributions of the NMR relaxation. While the exponent is unity for single-exponential relaxation, it decreases as the distribution of T_1^{-1} increases. As shown in Fig. 3(b), the observed exponents deviate from unity even at high temperatures. This deviation is due to two simple reasons. First, both for the inner and outer carbons, there are slightly different crystallographic sites and

the relaxation rates vary according to the site. This effect induces relaxation distributions even in a homogeneous system, explaining the observed suppression of β for the inner- ^{13}C single crystal. Second, these sites have anisotropic hyperfine couplings, which causes the relaxation rates to also vary with the angle between the sample direction and applied field. For the assemblage samples, this effect also contributes to the suppression of β , which is stronger for the inner ^{13}C assemblage than for outer ^{13}C assemblage.

The most important point is the further decrease in β from the high-temperature values. These decreases are observed below 20–25 K, where the VBS state set in. This result directly indicates that the relaxations in the VBS state become inhomogeneous, providing clear evidence that the additional relaxation appearing in the VBS state is not caused by the bulk mechanism that characterizes bulk spin excitations. Instead, it is caused by the orphan impurity spins, whose emergence is captured by the spectral results as explained in the previous section. (This conclusion is further supported also by the spectral position dependence of T_1^{-1} ; see the Supplemental Material [18].)

IV. GENERAL FORMALISM OF NMR T_1^{-1} CAUSED BY IMPURITY FREE SPINS

The orphan impurity spins in $\text{EtMe}_3\text{P}[\text{Pd}(\text{dmit})_2]_2$ can be regarded as free spins in the first approximation because they are diluted. (In fact, a susceptibility study reports that the magnitude of the Curie tail observed in the work corresponded to an $1/2$ spin per 3×10^2 formula units [12].) In this section, we present the general formalism of NMR T_1^{-1} originating from the dynamics of free $1/2$ -spins under a static magnetic field, aiming to establish a firm foundation for analyzing the low-temperature T_1^{-1} data presented in the previous section. In addition, it is noteworthy that T_1^{-1} caused by the free spins have been occasionally modeled [9,19] by the phenomenological Bloembergen-Purcell-Pound (BPP) model [20]. The formalism in this section validates the application of the phenomenological BPP model to the free spin system while also highlighting the applicability limitation of the BPP model. Specifically, in the low-temperature regime where $k_B T$ is smaller than the Zeeman gap of the free spins Δ , the original BPP model breaks down, necessitating the introduction of a correction factor that strongly depends on temperature. This correction factor becomes pivotal when discussing the low-temperature T_1^{-1} , e.g., in VBS states.

The NMR relaxation rate T_1^{-1} arises from internal magnetic field fluctuations perpendicular to an applied static magnetic field H_0 at the NMR frequency ω_n (typically ~ 1 mK). For free spin systems, these fluctuations are caused by spin dynamics and connected to the imaginary part of the dynamic spin susceptibility (of the free spins) through the fluctuation-dissipation theorem. At temperatures $k_B T \gg \hbar\omega_n$, the theorem gives

$$T_1^{-1} = \frac{2\gamma_n^2 k_B T}{(\gamma_e \hbar)^2} \left[|A_{\text{od}}|^2 \frac{\chi''_{\parallel}(\omega_n)}{\omega_n} + |A_{\perp}|^2 \frac{\chi''_{\perp}(\omega_n)}{\omega_n} \right], \quad (1)$$

where $\chi''_{\parallel,\perp}$ are the imaginary parts of the dynamic spin susceptibilities (of the free spins) parallel and perpendicular to

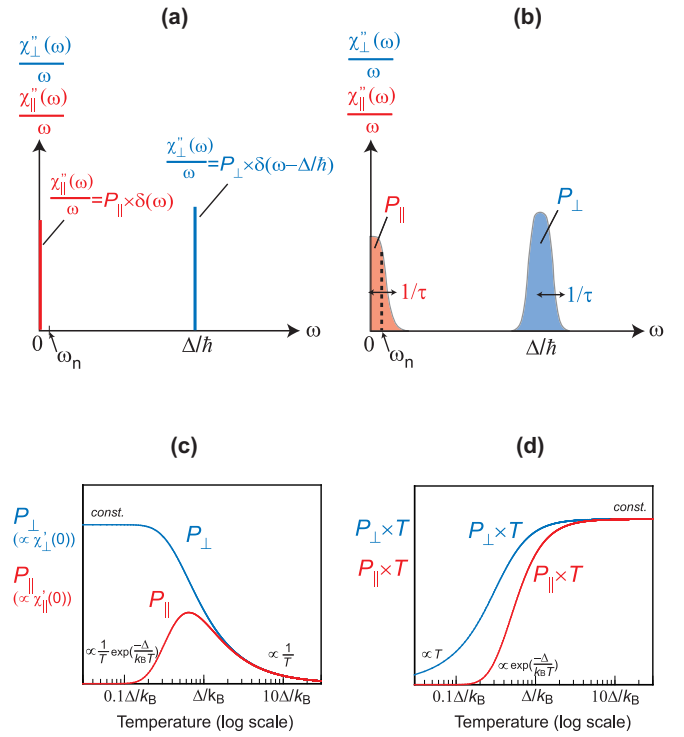


FIG. 4. (a) Imaginary parts of the dynamic spin susceptibilities over ω parallel and perpendicular to a static magnetic field H_0 for completely isolated free $1/2$ -spin systems with no external interactions. In this panel, Δ represents the Zeeman energy gap $g\mu_B H_0$, where g is the electron spin g -factor and μ_B is the Bohr magneton. $P_{\parallel}$ and $P_{\perp}$ represent the intensities of the parallel and perpendicular modes, respectively. (b) Imaginary parts of the dynamic spin susceptibilities over ω parallel and perpendicular to H_0 for free $1/2$ -spin systems in real materials with a finite lifetime τ . (c) Temperature dependence of $P_{\parallel}$ and $P_{\perp}$, which are proportional to $\chi'_{\parallel}(0)$ and $\chi'_{\perp}(0)$, respectively. In the low temperature region $k_B T \ll \Delta$, $\chi'_{\parallel}(0)$ exhibits an activation decrease, whereas $\chi'_{\perp}(0)$ maintains a constant value due to the Van Vleck susceptibility mechanism. (d) Temperature dependence of $P_{\parallel} \times T$ and $P_{\perp} \times T$.

H_0 , respectively. Note that $\chi''_{\parallel,\perp}$ represent the susceptibilities under H_0 , which are distinct from those under zero magnetic field; in other words, $\chi''_{\parallel,\perp}$ corresponds to *additional* responses to *additional* fields $[\delta H_{\parallel}(\omega)$ or $\delta H_{\perp}(\omega)]$ applied parallel and perpendicular to H_0 [21]. The coefficients $A_{\text{od},\perp}$ are the hyperfine form factors between a free spin and a nuclear spin: $A_{\perp}$ reflects the diagonal elements of the hyperfine tensor perpendicular to H_0 , and A_{od} reflects the off-diagonal elements of the hyperfine tensor between the parallel direction and the perpendicular directions to H_0 . These coefficients vary depending on the distance between the free spin and the nuclear spin, causing inhomogeneous relaxation.

Figures 4(a) and 4(b) show the imaginary parts of the dynamic spin susceptibilities divided by ω for free spins under H_0 . Because the perpendicular field perturbation $\delta H_{\perp}(\omega)$ induces the transition between the two Zeeman states of the free spins, $\chi''_{\perp}(\omega)/\omega$ exhibits a structure at the Zeeman frequency $\Delta/\hbar$. In contrast, $\chi''_{\parallel}(\omega)/\omega$ exhibits a structure only at $\omega \sim 0$ (quasielastic mode) because the parallel field perturbation $\delta H_{\parallel}(\omega)$ does not induce the transition. In the case of

completely isolated free spins, the lifetime of the Zeeman states is infinite and thus the structures are delta functions with the intensities of $P_{\parallel}$ and $P_{\perp}$, as shown in Fig. 4(a). However, free spins in real materials have a finite lifetime τ , which results in Lorentzian-type broadening as shown in Fig. 4(b). Because the Zeeman gap of the free spins Δ is much larger than $\hbar\omega_n$, T_1^{-1} is dominated by the quasielastic mode in the parallel dynamics, not influenced by the perpendicular dynamics, when $1/\tau \ll \Delta/\hbar$.

In this case,

$$T_1^{-1} = \frac{4\gamma_n^2 k_B}{\pi(\gamma_e \hbar)^2} |A_{\text{od}}|^2 (P_{\parallel} T) \frac{\tau}{1 + \omega_n^2 \tau^2}. \quad (2)$$

Therefore, the temperature dependence of the T_1^{-1} caused by the free spins is determined from the temperature dependence of $P_{\parallel} \times T$ and τ .

P is proportional to $\chi'(0)$ because of the Kramers-Kronig relation ($\int_0^{\infty} \chi''_{\perp, \parallel}(\omega)/\omega d\omega \propto \chi'_{\perp, \parallel}(0)$). In the high-temperature region $k_B T \gg \Delta$, $\chi'(0)$ is inversely proportional T , resulting in $P_{\parallel} \times T$ being constant as shown in Fig. 4(d). Consequently, Eq. (2) is reduced to the phenomenological BPP model, which is often adopted as the model to describe free spin dynamics [9,19]. In the low-temperature region $k_B T \ll \Delta$, however, $P_{\parallel} \times T$ exhibits an activation decrease with the Zeeman gap Δ , owing to the saturation of the polarization. Hence, T_1^{-1} generally should exhibit an activation decrease at sufficiently low temperatures, regardless of the behavior of $1/\tau$.

The temperature dependence of $1/\tau$ is not trivial. The primary factor that determines $1/\tau$ is likely interaction between free spins and phonons under spin-orbit coupling, as well as interaction between free spins and bulk electron spins, although the latter is irrelevant in the case of bulk gapped systems. Additionally, at very low temperatures, it is likely influenced also by slight but nonzero interaction among free spins themselves. For VBS states, it is reasonable to expect that $1/\tau$ exhibits a rapid decrease as the temperature decreases because of the reduction in the number of excited phonons with the Zeeman energy Δ . At absolute zero, $1/\tau$ is expected to saturate to a very small but nonzero value probably dominated by the interaction between free spins themselves, which is negligible compared to Δ but can be comparable to $\hbar\omega_n$.

V. DISCUSSION OF T_1^{-1} OF $\text{EtMe}_3\text{P}[\text{Pd}(\text{dmit})_2]_2$ AT LOW TEMPERATURES

As discussed previously, the observed T_1^{-1} [Fig. 3(a)] of $\text{EtMe}_3\text{P}[\text{Pd}(\text{dmit})_2]_2$ below ~ 10 K is attributable to orphan impurity spins. Having formulated the problem and derived Eq. (2), where T_1^{-1} is determined by the product of $P_{\parallel} \times T$ and the Lorentzian term with a width of $1/\tau$, we can explore the detailed mechanism behind the observed T_1^{-1} . Note that the applied magnetic field in all measurements was 7.65 T, corresponding the Zeeman energy temperature Δ/k_B of ~ 10 K.

The observed T_1^{-1} exhibits a tendency to decrease at low temperatures, as shown in Fig. 3(a). This is primarily attributed to the monotonous decrease in $P_{\parallel} \times T$ below $\sim \Delta/k_B$ shown in Fig. 4(d). However, the observed decreases in T_1^{-1} are not monotonous; all three samples exhibit humplike

structures in T_1^{-1} at 3–4 K, although the prominence of these structures varies. Because $P_{\parallel} \times T$ exhibits a monotonous decrease below $\sim \Delta/k_B$, the hump-like structures are attributable to the effect of the other Lorentzian term, that is, the slowing down of τ . When $1/\tau$ decreases to ω_n , the Lorentzian term exhibits a broad peak. Therefore, our result clearly captures the slowing down of $1/\tau$. Note that the slowing down scenario of $1/\tau$ for impurity spin dynamics has already been pointed out by Pustogow and coworkers in other organic compounds [9,19]. In addition, the hump temperatures for the three samples, corresponding to the temperature where $1/\tau$ becomes equal to ω_n , are nearly identical among the three samples. This suggests that $1/\tau$ does not depend on the sample. The difference in the data among the three samples lies only in the varying magnitudes of the structures, likely attributable to the different concentrations of the orphan impurity spins and also possibly to the different off-diagonal elements of the interaction tensors between the orphan impurity spins and the nuclear spins.

VI. CONCLUDING REMARKS AND FUTURE WORKS

In summary, we have reported the ¹³C NMR spectra and T_1^{-1} for the three samples of $\text{EtMe}_3\text{P}[\text{Pd}(\text{dmit})_2]_2$, which is a representative organic VBS system. The spectra exhibit inhomogeneous broadening below the VBS transition temperature of 25 K, indicating the appearance of orphan impurity spins at sites where dimerization fails to occur. Below 25 K, T_1^{-1} for the three samples exhibits a rapid decrease, which is attributable to the formation of a spin gap. However, at even lower temperatures, the behavior of T_1^{-1} deviates positively from the expected activation decrease. Simultaneously, in this temperature region, the stretching exponents of the relaxation curves also exhibit a considerable decrease. These observations clearly capture that the dynamics of the orphan impurity spins dominates the NMR relaxations at low temperatures. Furthermore, we have organized the general formalism for describing T_1^{-1} caused by the dynamics of free spins and concluded that the temperature dependence of the observed T_1^{-1} in the low-temperature region is explained by the two factors: the decrease in $P_{\parallel} \times T$ characterized by the electron Zeeman gap and the slowing down of τ .

This comprehensive report and analysis will provide a solid foundation for future research discussing NMR results of QSL candidate materials, facilitating comparisons between the results of the QSL candidates and the present results of the representative VBS system. Lastly, we provide preliminary comparisons between the previously reported NMR results of the two organic QSL candidates $[\kappa\text{-(BEDT-TTF)}_2\text{Cu}_2(\text{CN})_3]$ and $\text{EtMe}_3\text{Sb}[\text{Pd}(\text{dmit})_2]_2$ and the present results, although the final conclusion is left to future studies.

The NMR relaxation behavior of $\kappa\text{-(BEDT-TTF)}_2\text{Cu}_2(\text{CN})_3$ [2,7] is indeed similar to the present results, as already pointed out by Pustogow and coworkers [9,19]. $\kappa\text{-(BEDT-TTF)}_2\text{Cu}_2(\text{CN})_3$ exhibits a humplike structure in T_1^{-1} at low temperatures, accompanied by a decrease in the stretching exponent. The apparent difference between $\kappa\text{-(BEDT-TTF)}_2\text{Cu}_2(\text{CN})_3$ and $\text{EtMe}_3\text{P}[\text{Pd}(\text{dmit})_2]_2$ lies in the magnitude of the humplike structures in T_1^{-1} . However, such magnitude difference is also observed among the

three samples in the present paper. Thus, it may not be an essential difference but rather attributable to variations in the concentration of impurity spins. Consequently, the reported T_1^{-1} of κ -(BEDT-TTF) $_2$ Cu $_2$ (CN) $_3$ is also possibly influenced by the impurity spins, as suggested by Pustogow and coworkers. The remaining question for the impurity-relaxation scenario is the discrepancy in the temperature dependence of T_1^{-1} ; the reported T_1^{-1} values in κ -(BEDT-TTF) $_2$ Cu $_2$ (CN) $_3$ exhibit power-law decreases at ultra-low temperatures, whereas the theoretical T_1^{-1} caused by the impurity spins should still exhibit an activation decrease with the Zeeman gap at ultralow temperatures, as explained in the general formalism section. We are not entirely certain whether this discrepancy is a serious problem for the impurity-relaxation scenario in κ -(BEDT-TTF) $_2$ Cu $_2$ (CN) $_3$ because the relaxation curves in κ -(BEDT-TTF) $_2$ Cu $_2$ (CN) $_3$ at ultralow temperatures are highly inhomogeneous, resulting in ill-defined T_1^{-1} values.

In contrast, the NMR relaxation behavior of EtMe $_3$ Sb[Pd(dmit) $_2$] $_2$ [16,22] appears to differ from the present results. At temperatures above ~ 1 K, T_1^{-1} in EtMe $_3$ Sb[Pd(dmit) $_2$] $_2$ does not display a noticeable abrupt drop, whereas the stretching exponents exhibit gradual

decreases below ~ 10 K, likely associated with the recently observed disordered Mott nature [23] and/or glassy phonon behavior [24]. Remarkably, T_1^{-1} exhibits a steep decrease below ~ 1 K, which, at first glance, resembles the T_1^{-1} decreases observed in this study due to the VBS transition. However, the stretching exponents in EtMe $_3$ Sb[Pd(dmit) $_2$] $_2$ recover to uniform-relaxation values again below ~ 1 K, representing a sharp contrast to the VBS behavior observed in this study, where the stretching exponents significantly decrease in the VBS state. Further studies to explore the underlying causes of this difference are highly desired. Such studies will give a clue to unraveling the ground-state nature of EtMe $_3$ Sb[Pd(dmit) $_2$] $_2$, which is currently subject to considerable debate [16,22,24–37].

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