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Static and dynamic interaction between π and d electrons in organic superconductor β''-(BEDT-TTF)$_4$[$(H_3O)Fe(C_2O_4)_3$] · C_6H_5Br studied by ^{13}C NMR spectroscopy

Y. Ihara,[1,*] Y. Futami,[1] A. Kawamoto,[1] K. Matsui,[2] T. Goto,[2] T. Sasaki,[3] S. Benmansour,[4] and C. J. Gómez-García[4]

[1]*Department of Condensed Matter Physics, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan*

[2]*Department of Physics, Sophia University, Kioi-cho, Chiyoda-ku, Tokyo 102-8554, Japan*

[3]*Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*

[4]*Instituto de Ciencia Molecular, Parque Científico, Universidad de Valencia, 46980 Paterna, Valencia, Spain*

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We present the results of ^{13}C NMR experiments in an organic superconductor with localized Fe spins β''-(BEDT-TTF)$_4$[$(H_3O)Fe(C_2O_4)_3$] · C_6H_5Br. We reveal the antiferromagnetic coupling between Fe d spins and π spins, which creates an exchange field antiparallel to the external field direction at the π electrons. In addition to the static effects of Fe spins, we show from the nuclear spin-lattice relaxation rate measurement that the magnetic fluctuations generated by Fe spins are suppressed at low temperatures and high magnetic fields. These conditions are suitable to stabilize the field-induced superconductivity by the field compensation mechanism. After the suppression of Fe-spin dynamics by a magnetic field of 19 T, we observed the underlying π-electron contribution. We discuss a possible anomaly in the π-electron system.

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I. INTRODUCTION

Magnetic scattering by magnetic ions in superconductors breaks Cooper pairs and violates the superconducting state. In some superconductors, however, magnetic ions support superconductivity by creating an exchange field antiparallel to the external field and thus compensating the field effects. This compensation mechanism was theoretically proposed by Jaccarino and Peter [1]. To realize such a situation experimentally, two conditions should be achieved. One is that the exchange interaction between itinerant conduction electrons and localized magnetic moments should stabilize an antiparallel spin configuration. The second condition is that the magnetic moments have to create a static exchange field to minimize the pair breaking effect by fluctuating magnetic fields. When these conditions are satisfied, superconductivity will be stabilized, rather than suppressed, by magnetic fields, and a field-induced superconducting state will be observed.

Two materials are known at this time as candidates for a field-induced superconductor by compensation mechanism. The first example is the Chevrel phase superconductor $Eu_{1-x}Sn_xMo_6S_8$ [2]. In this material, field-induced superconductivity was observed either under hydrostatic pressures [3], or in a sample with partially substituted Se for S [4]. The exchange coupling between the conduction electrons in the three-dimensional (3D) network and the Eu moments isolated from it was revealed to be antiparallel from microscopic experiments [5]. In a sample with an appropriate Sn concentration, which shows an optimal superconducting transition temperature T_c of approximately 4 K, the superconducting state is once suppressed to 0 K at 1 T, and then the field-induced superconducting state appears above 5 T. The negative exchange field can eliminate the Pauli pair breaking effect, but the orbital effect should still suppress superconductivity in a 3D electron system. Therefore, a low-dimensional material with a high orbital limiting field is suitable to realize a field-induced superconducting state. In the layered organic superconductor λ-$(BETS)_2X$ [BETS stands for bis(ethylene)dithio-tetraselenafulvalene, and X stands for monovalent anions, $FeCl_4$ or $GaCl_4$], the conducting carriers are doped from the insulating anion layers to the conducting BETS layers, and construct a two-dimensional (2D) electronic structure [6,7]. Therefore, the orbital pair breaking effect should be small when the field is parallel to the conduction plane. In fact, highly anisotropic behavior was reported for the upper critical field B_{c2} in the nonmagnetic λ-$(BETS)_2GaCl_4$ salt [8]. When the field is applied parallel to the conduction plane, B_{c2} reaches 14 T, which is four times larger than the B_{c2} for a perpendicular direction. In the magnetic λ-$(BETS)_2FeCl_4$ salt, conduction electrons are weakly coupled to the localized Fe spins located on the insulating layer. The field-induced superconducting state was observed below 4 K in the field range between 20 and 40 T [9,10]. The antiparallel exchange interaction was confirmed from ^{77}Se NMR spectroscopy, and the strength of the exchange field was estimated as approximately 30 T for a fully polarized Fe-spin moment of $5\mu_B$ [11–13]. The good agreement between the field range that shows field-induced superconductivity and an exchange interaction strongly suggests the compensation mechanism for λ-$(BETS)_2FeCl_4$.

The static component of the exchange interaction was estimated, but the dynamics of localized Fe spins in λ-$(BETS)_2FeCl_4$ has not been revealed yet. Fe spins should be fully polarized in a high magnetic field limit. However, as the magnetization measurement revealed a Weiss temperature of -15 K [7,14], the interaction between Fe spins would generate fluctuations even at a field range of 30 T and low temperatures, and thus scatter the Cooper pairs. The dynamics of localized spins should be investigated to confirm the compensation mechanism.

The nuclear spin-lattice relaxation rate measurement by NMR experiments is one of the best techniques to probe the dynamics of localized Fe spins. Such a measurement has not been done in λ-$(BETS)_2FeCl_4$ because this salt crystallizes into a thin needle shape, and thus the small

*yihara@sci.phys.hokudai.ac.jp

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sample mass limits the signal-to-noise ratio. The single crystals of another layered organic superconductor with Fe spins, β''-(BEDT-TTF)$_4$[(H$_3$O)Fe(C$_2$O$_4$)$_3$] $\cdot$ C$_6$H$_5$Br (β''-Fe) salt, were reported to be much larger in size [15]. [Here, BEDT-TTF stands for bis(ethylenedithio)-tetrathiafulvalene.] Therefore, the NMR experiment should be performed for the β''-Fe salt. The superconducting transition of the β''-Fe salt was observed at $T_c = 4$ K from a resistivity measurement at zero field, and disappears by applying a field of 8 T [15]. A resistivity measurement in high magnetic fields has not been performed. A sister compound without a magnetic ion, β''-(BEDT-TTF)$_4$[(H$_3$O)Ga(C$_2$O$_4$)$_3$] $\cdot$ C$_6$H$_5$NO$_2$ (β''-Ga) salt, shows superconductivity at $T_c = 7.5$ K [16]. From the resistivity measurement for β''-Ga salt, B_{c2} was determined as 32 T when the field is in the conducting plane [17]. The extremely high B_{c2} shows a weak orbital pair breaking effect for β''-type BEDT-TTF superconductors, rendering them suitable to exhibit field-induced superconductivity by the compensation mechanism in the β''-Fe salt. The bulk magnetization measurement shows a Curie-like temperature dependence, which is understood as a nearly free Fe-spin contribution with $S = 5/2$ [15]. The exchange interaction between this localized Fe spin and conducting π electron should be measured by a microscopic probe. Therefore, we performed ^{13}C NMR measurements on a single crystal of the β''-Fe salt and investigated the microscopic interaction between the Fe spins and the π electrons, and also the dynamics of the Fe spins in magnetic fields.

II. EXPERIMENT

The single crystals of β''-Fe salt were grown with the electrochemical oxidation process [15]. The dimension of the obtained single crystal is $2\times1\times0.5$ mm^3. We used an asymmetric BEDT-TTF molecule, for which only one side of the central C=C bond is enriched with a ^{13}C isotope [18]. With these molecules, we can eliminate the spectrum splitting by nuclear spin-spin coupling [19]. The external fields were applied along the b direction. The field orientation was controlled by a single axis rotator. We performed the NMR experiment at 19 T at the High Field Laboratory for Superconducting Materials, Institute for Materials Research, Tohoku University. The electron spin resonance (ESR) experiment was performed at the Institute for Molecular Science.

III. RESULTS AND DISCUSSION

A. Static exchange interaction

We obtained the NMR spectra in magnetic fields of 6.19 and 2.88 T applied along the b axis. This compound consists of two crystallographically independent BEDT-TTF molecules in a unit cell, and each molecule possesses two independent ^{13}C sites. Therefore, four NMR peaks from every ^{13}C site should be observed. As shown in Fig. 1, however, we observed a single NMR peak at 150 K, which suggests that the local environment around the four ^{13}C sites is almost equivalent so as to merge the four peaks into a single peak. The horizontal axis in Fig. 1 is the NMR shift, which is defined as the shift of NMR frequency from the reference material (tetramethylsilene: TMS). At low temperatures the NMR spectra shift to low frequencies

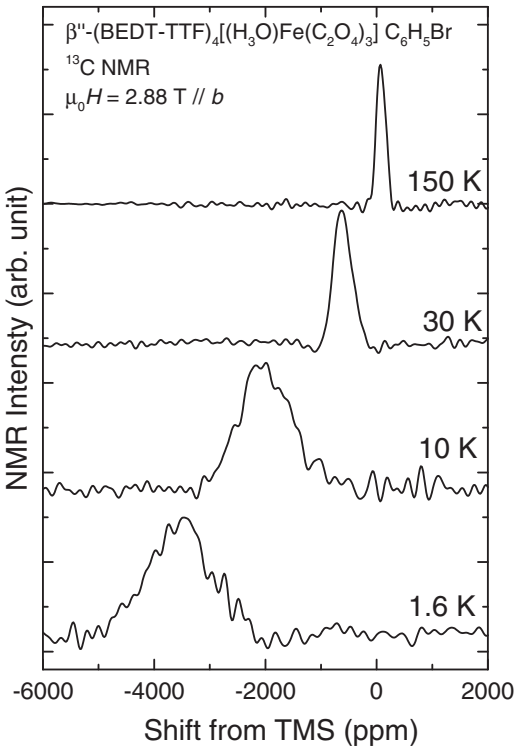

FIG. 1. Temperature dependence of ^{13}C NMR spectra in magnetic fields of 2.88 T applied along the b axis. A large shift and broadening were observed at low temperatures because of the large magnetization of Fe spins.

by 4000 ppm at 2.88 T, and 2000 ppm at 6.2 T, and the linewidth becomes as large as 1000 ppm. In most BEDT-TTF based superconductors, the typical NMR shift originating from the paramagnetic π spins is less than 1000 ppm, and is weakly temperature dependent. In fact, the NMR shift of the sister compound β''-Ga salt along the b axis was measured as approximately 200 ppm [20,21]. The huge temperature dependence indicates that the magnetic properties at the ^{13}C sites are dominated by the magnetism of the localized Fe spins.

Figure 2 shows the temperature dependence of the NMR shift δ determined by fitting the spectra with Lorentzian functions. An identical temperature dependence was observed at 2.88 and 6.19 T at high temperatures. But, the NMR shift at 6.19 T levels off below 15 K, while δ at 2.88 T shows a large temperature dependence down to 3 K. As δ is proportional to the magnetization divided by field M/H, the temperature dependence of δ becomes small when the Fe spins are fully polarized at low temperatures and high fields.

The large Fe-spin contribution should be subtracted from the total δ to investigate the magnetic properties of the π electrons in the BEDT-TTF molecular orbital. The localized Fe spins generate a local magnetic field at the ^{13}C site by two different interactions: the direct dipole interaction and the indirect transfer interaction through the π electrons. We refer to the former direct contribution as the NMR shift due to the Fe spins $\delta_{\rm Fe}$, and assume that the latter contribution is included in the NMR shift due to the π spins δ_π. The total δ is written in terms of $\delta_{\rm Fe}$, δ_π, and the chemical shift σ as

$$\delta = \delta_\pi + \delta_{\rm Fe} + \sigma. \quad (1)$$

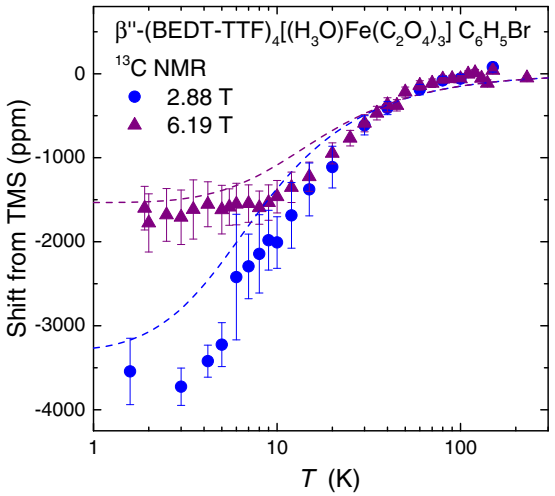

FIG. 2. Temperature dependence of the NMR shift at magnetic fields of 6.19 T and 2.88 T. Dashed lines represent the simulated temperature dependence originating from free Fe spins.

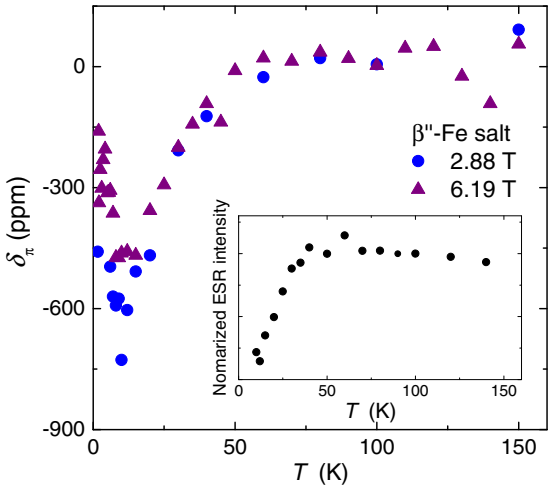

FIG. 3. Temperature dependence of the NMR shift by π spins δ_π. The decrease in δ_π observed below 50 K is explained by the negative exchange interaction between Fe and π spins. The inset shows the temperature dependence of ESR intensity. The decrease in ESR intensity was observed also below 50 K. This consistent behavior evidences the validity of our analysis to extract δ_π.

The chemical shift is specific to the BEDT-TTF molecule and depends only on the valence of the molecule. We used a chemical shift tensor for $0.5e$, which was measured in α-(BEDT-TTF)$_2$I$_3$ [22], to calculate σ for β''-Fe salt, and obtained $\sigma = 85$ ppm when the field is parallel to the b direction.

A direct Fe-spin contribution $\delta_{\rm Fe}$ can be estimated using the uniform susceptibility $\chi_{\rm Fe}$. In the β''-Fe salt, a magnetic susceptibility measurement has revealed that the Weiss temperature is as small as -0.08 K [15]. The weak Fe-Fe interaction can be understood by the long Fe-Fe distances of 11.3 and 10.3 Å. As the Fe spins are almost isolated, we approximate the temperature and field dependence of $\chi_{\rm Fe}$ originating from the Fe spin $S = 5/2$ to the Brillouin function $B_J(x)$. Then, $\chi_{\rm Fe}$ is written as

$$\chi_{\rm Fe} = \frac{Ng\mu_B S B_J(x)}{H}, \tag{2}$$

where N and g are the number of Fe spins, and the g factor of them, and $x = gS\mu_B H/k_{\rm B}T$. The dipole coupling between Fe spins and a ^{13}C nuclear spin was calculated as $A_{\rm dip} = -20$ mT/μ_B by integrating the dipole field from Fe spins located within 200 Å from the target ^{13}C site. The Lorentz correction of 0.17 mT/μ_B is included in this calculation. An ellipsoidal sample shape was assumed to correct the demagnetization effect. As we observed a single ^{13}C NMR peak, we averaged $A_{\rm dip}$ for the four crystallographically independent ^{13}C sites. Using this coupling constant, $\delta_{\rm Fe}$ is written as

$$\delta_{\rm Fe} = \frac{A_{\rm dip}}{N\mu_0\mu_B}\chi_{\rm Fe} = gSA_{\rm dip}\frac{B_J(x)}{\mu_0 H}, \tag{3}$$

and the calculated temperature dependence of $\delta_{\rm Fe}$ at each field strength is represented in Fig. 2 as dashed lines. The good agreement with the experimental data confirms that the Fe-spin contribution dominates the temperature dependence of the NMR shift. The π contribution δ_π is responsible for the deviation from the dashed line.

The magnetism of π spins can be investigated by subtracting $\delta_{\rm Fe}$ and σ from the total NMR shift δ. As shown in Fig. 3, δ_π is nearly temperature independent above 50 K, and decreases at low temperatures. At high temperatures, where the Fe-spin magnetization is small, δ_π is small and positive, which is consistent with the positive and almost-temperature-independent δ_π observed in the β''-Ga salt [20,23]. The strong temperature dependence of δ_π in the β''-Fe salt can be attributed to the negative contribution from the Fe spins.

The suppression of π-spin magnetization was also observed by the electron spin resonance (ESR) measurement (inset of Fig. 3). A sharp ESR signal from the π spins can be differentiated from the broad ESR signal of Fe spins, which is typical for large spins with dipole coupling [15]. The ESR signal intensity of π spins decreases below 50 K, which indicates the reduction of π-spin magnetization at low temperatures. This behavior is consistent with the temperature dependence of δ_π obtained above, and thus confirms that the suppression of δ_π below 50 K is not an artifact originating from the $\delta_{\rm Fe}$ subtraction procedure. The suppression of π-spin magnetization was interpreted as the spin gap formation in the π spins below 50 K [15]. In this study we will explain this behavior without such a gap at 50 K by introducing the exchange interaction between π and Fe spins.

An abrupt increase in δ_π was observed below 10 K. At the same temperature, ESR intensity completely disappears. We suggest that a gap in the π-electron system opens below this temperature. As the nonmagnetic β''-Ga salt shows a charge ordering transition at 8.5 K [20,21], the anomaly at 10 K would be related to the charge instability.

Hereafter, we focus on the suppression of δ_π above 10 K. The magnetization of the π spin $M_\pi(H,T)$ polarized by the external field H and the exchange field from the Fe spins $JM_{\rm Fe}(H,T)$ can be written as

$$M_\pi(H,T) = \chi_\pi(T)[H + JM_{\rm Fe}(H,T)]. \tag{4}$$

This π-spin magnetization creates a hyperfine field at the ^{13}C site through a hyperfine coupling constant A_π, and causes a NMR frequency shift δ_π. The hyperfine field B_π is therefore

$$B_\pi(H,T) = \frac{A_\pi}{N\mu_B}\chi_\pi(T)[H + JM_{\rm Fe}(H,T)] = \delta_\pi(H,T)\mu_0 H. \quad (5)$$

This relation suggests that the temperature dependence of either χ_π or $M_{\rm Fe}$ is responsible for the suppression of δ_π. As the temperature dependence of χ_π is weak above 10 K in the nonmagnetic β''-Ga salt, in which χ_π can be measured directly, we assume a weak temperature dependence of χ_π also for the β''-Fe salt. Therefore, the reduction of δ_π is due to the $JM_{\rm Fe}$ term, where $M_{\rm Fe}$ follows the Curie-like temperature dependence. This $JM_{\rm Fe}$ term will reduce δ_π only if J is negative, creating an internal field antiparallel to the external field direction. Thus, $M_\pi = \chi_\pi H_{\rm eff}$ decreases because the external field is compensated by the internal one.

The strength of the exchange field from the Fe spins can be estimated from Eq. (5). In Fig. 4, we plot B_π experimentally measured from δ_π at 6.19 and 2.88 T as a function of calculated $M_{\rm Fe}$, using the temperature as an implicit parameter. The negative slope observed in both fields evidences the negative sign for the exchange interaction J. The strength of the exchange field created by one Bohr magneton $B_{\rm ex}$ is calculated by fitting the results shown in Fig. 4 to Eq. (5), and we obtained $B_{\rm ex} = -11(2)$ T for both fields. Therefore, when the Fe spins are fully polarized by strong external fields, the π electrons feel the exchange field of 55 T antiparallel to the external field direction. These estimates of J are the upper limit as we omitted the temperature dependence of χ_π. If χ_π is also temperature dependent, and becomes small at low temperatures, the absolute value of J would also become smaller.

In the case of λ-$(BETS)_2FeCl_4$ salt, the strength of the exchange field was estimated as 32 T [13]. Even though the $[Fe(C_2O_4)_3]^{3-}$ complex is larger in size than the $(FeCl_4)^-$ ion, the exchange between Fe ions and BEDT-TTF molecules is stronger in the β''-Fe salt because the $[Fe(C_2O_4)_3]^{3-}$ complex forms numbers of hydrogen bonds to the hydrogens at the ethylene end group with an O-H distance of approximately 2.5 Å, whereas in the λ-$(BETS)_2FeCl_4$ salt, only one Cl-H bond has a bond length of approximately 3 Å, which is comparable to the sum of the van der Waals radii for Cl and H.

The exchange interaction in the Kondo impurity systems is typically in the order of a few eV, whereas J of approximately 50 T/5μ_B observed in the β''-Fe salt corresponds to a few meV. The exchange interaction in the organic conductors is extremely small because of the layered structure, and therefore the exchange interaction can be compensated by the external fields accessible with high-field pulsed magnets. Resistivity measurements under high fields corresponding to the estimated exchange interaction will be performed.

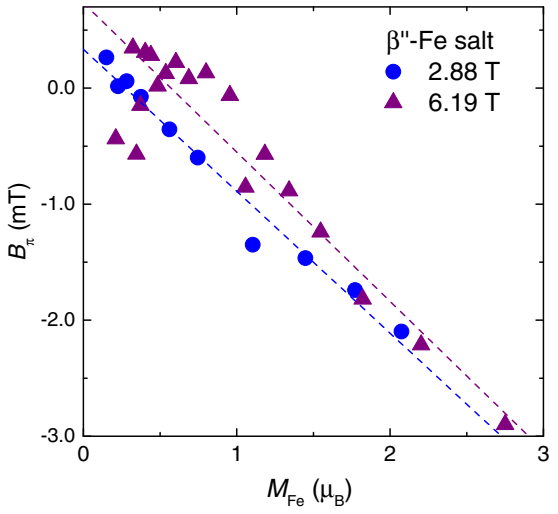

FIG. 4. The hyperfine field from π electrons B_π plotted as a function of the magnetization of Fe spins $M_{\rm Fe}$. The negative slope indicates the negative exchange interaction as expressed by Eq. (5).

B. Dynamics of the localized spin

We have measured the nuclear spin-lattice relaxation rate $1/T_1$ at the ^{13}C site in order to study the dynamics of the Fe spins. All the temperature and field dependence of $1/T_1T$ is explained by the dominant Fe-spin contribution and a small π-electron background. Figure 5 shows the temperature dependence of $1/T_1T$ measured with three different fields applied parallel to the b axis. The absolute value of $1/T_1T$ is suppressed by high fields following almost an H^{-2} dependence. This field dependence suggests a Lorentzian-type ω dependence for the dynamic susceptibility $\chi''(\omega)$. At the highest field of 19 T, $1/T_1T$ becomes as small as the value obtained in the β''-Ga salt, $1/T_1T \simeq 0.01$ s^{-1} K^{-1}, and therefore the contribution from the conduction electrons should be taken into account, whereas at the lowest field of 2.88 T, the π-electron contribution is negligible. We first

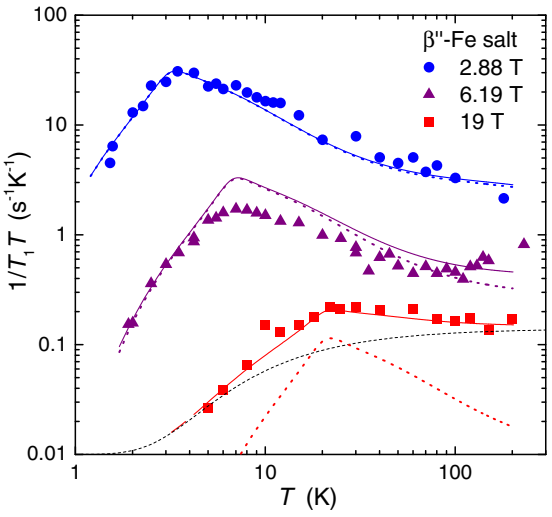

FIG. 5. Temperature dependence of $1/T_1T$ in three different fields. $1/T_1T$ is strongly suppressed in high magnetic fields. The solid lines are the result of our model calculation. The temperature and field dependence can be explained by our model. The dotted and dashed lines represent the Fe-spin contribution and the underlying π contribution, respectively.

analyze the results at low field to investigate the dynamics of the localized Fe spins.

In general, $1/T_1$ is written in terms of the dynamic susceptibility of Fe spins at the NMR frequency $\chi''(\omega_0)$ as

$$\frac{1}{T_1} = \frac{2\gamma_n^2 k_B T}{(g\mu_B)^2}(A_{\rm dip}^{\perp})^2 \frac{\chi''(\omega_0)}{\omega_0}. \quad (6)$$

Here, we assume that a local magnetic fluctuation at the ^{13}C site is generated by the dipole fields from the Fe spins, and a Lorentzian-type ω dependence for $\chi''(\omega)$ centered at the Larmor frequency of the localized spin ω_e. The temperature and field dependence can be characterized by the field derivative of the Brillouin function, B_J'. Then the above equation becomes

$$\frac{1}{T_1} = \frac{2\gamma_n^2 k_B T}{(g\mu_B)^2}(A_{\rm dip}^{\perp})^2 \frac{B_J'}{\omega_0} \frac{\omega_e \tau}{1+\omega_e^2\tau^2}. \quad (7)$$

Here, we neglected ω_0 in the last term as $\omega_e \gg \omega_0$. From this equation, the Fe-spin correlation time τ can be measured experimentally.

The temperature dependence of $1/\tau$ at 2.88 T is shown in Fig. 6, in which the horizontal axis is the reduced temperature $t = k_B T/\mu_B H$. The calculated $1/\tau$ of approximately 50 ns^{-1} corresponds to the energy scale of 1 K. Our result is thus consistent with the weak Fe-spin correlation measured by the bulk susceptibility [15]. At high temperatures, $1/\tau$ follows a linear T dependence, which is characteristic of the localized moments coupled to the conduction electrons, such as CuMn dilute alloys [24]. A peak behavior was observed at low temperatures, where the thermodynamic energy becomes comparable to the Zeeman energy. This peak can be explained by the nuclear spin relaxation process originating from indirect coupling, that is, the coupling between ^{13}C nuclear spins and Fe spins through the conducting π electrons [25]. Two kinds of processes have been suggested by Benoit–de Gennes–Silhouette (BGS process) [26] and Giovannini-Heeger (GH process) [27]. The BGS process coincides with the Fe-spin flip, and has a large contribution at high temperatures, where the Fe spins are thermally excited, whereas the GH process has a dominant contribution at low temperatures, because this process involves virtual excitation, which does not modify the Fe spin. At the intermediate temperature of $k_B T \simeq \mu_B H$, both processes have a finite contribution, which gives rise to a peak in the total nuclear relaxation rate, and thus the peak in $1/T_1 T$. In the present framework, as $1/\tau$ is calculated from Eq. (7), which takes only the direct dipole interaction into account, a peak in $1/T_1 T$ caused by the additional nuclear spin relaxation processes results in the peak in $1/\tau$. When the temperature is much smaller than the Zeeman energy, τ becomes longer, which strongly suggests that the dynamics of Fe spins slows down to suppress the magnetic fluctuations at the conducting layers.

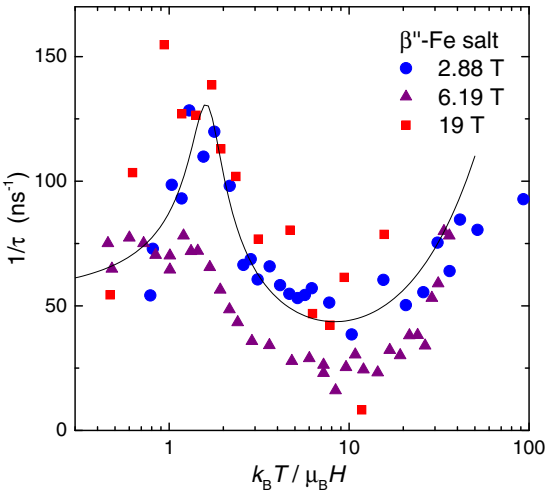

FIG. 6. Temperature dependence of Fe spin-spin correlation rate $1/\tau$ derived from $1/T_1 T$ measured at the ^{13}C site. The horizontal axis is the temperature normalized by the magnetic field $t = k_B T/\mu_B H$. The solid line is the fit to the data by Eq. (8).

To investigate the field dependence of $1/T_1 T$, we fit the t dependence of $1/\tau$ at 2.88 T with an empirical function with two terms,

$$\frac{1}{\tau} = \frac{70}{\sqrt{|t-1.6|}} + 2t \ ({\rm ns}^{-1}), \quad (8)$$

which is shown in Fig. 6 as a solid line. The diverging behavior at $t = 1.6$ is rounded by introducing a small dumping factor. Using this equation and Eq. (8), $1/T_1 T$ at 6.19 and 19 T were calculated and shown as the dotted lines in Fig. 5. Although the result for 6.19 T fits the temperature dependence of $1/T_1 T$, that for 19 T is much smaller than the experimentally obtained $1/T_1 T$ at 19 T. To explain the $1/T_1 T$ at high fields, we need to add the field-independent π-electron contribution. As the peak behavior at 20 K is consistently explained by the Fe-spin contribution, we introduce a weakly temperature-dependent term for the π-electron contribution,

$$\left(\frac{1}{T_1 T}\right)_{\pi} = 0.01 + 0.13 \exp\left(-\frac{10}{T}\right) ({\rm s}^{-1}\,{\rm K}^{-1}). \quad (9)$$

This underlying π-electron contribution is represented in Fig. 5 as a dashed line. The solid lines, which are the sums of the Fe-spin and π-electron contributions, fit well to the experimental data.

Now, we can calculate $1/\tau$ for 6.19 and 19 T by subtracting the π-electron contribution [Eq. (9)] from the observed $1/T_1 T$ and applying Eq. (7) to the remaining Fe-spin contribution. The results shown in Fig. 6 confirm that $1/\tau$ follows the universal t dependence written by Eq. (8). Therefore, in high magnetic fields and low temperatures, τ becomes long to suppress completely the dynamics of the Fe spins. This situation is ideal to stabilize the field-induced superconductivity, as the pair breaking effect by the fluctuating magnetic fields is eliminated. For the π-electron contribution, we introduced a thermal activation-type temperature dependence with a gap energy of 10 K, which suggests that the π-electron system is gapped at low temperatures. This result is consistent with the anomaly in the NMR shift, and the absence of the ESR spectrum below 10 K.

IV. CONCLUSION

We have performed ^{13}C NMR experiments at various fields up to 19 T. From the temperature dependence of the NMR

shift, we found that the exchange field created by the Fe spins to the conduction electrons is antiparallel to the external field direction, and its strength is approximately 55 T. The large exchange field antiparallel to the external field leads us to expect a field-induced superconducting state in high fields. The dynamics of the Fe spins was analyzed from the temperature and field dependence of $1/T_1T$. The correlation time between the Fe spins shows a peak at a temperature where the Zeeman energy becomes comparable to the thermal one. Below this temperature, the Fe-spin dynamics is strongly suppressed, meaning that in high magnetic fields the magnetic fluctuations will be sufficiently suppressed, and superconductivity could appear. The temperature dependence of $1/T_1T$ at 19 T shows an underlying contribution from the π electrons, which are gapped below 10 K. This result, together with the NMR shift and ESR spectra, suggests an anomaly in the π-electron system, which could be a charge ordering as observed in the sister compound β''-Ga salt. The details of the π-electron state will be investigated by NMR experiments at higher magnetic fields.

ACKNOWLEDGMENTS

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