

Microscopic observation of superconducting fluctuations in κ -(BEDT-TTF)₂Cu[N(CN)₂]Br by ¹³C NMR spectroscopy

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We performed ¹³C-NMR experiment and measured spin-lattice relaxation rate divided by temperature $1/T_1T$ near the superconducting (SC) transition temperature T_c in κ -(BEDT-TTF)₂Cu[N(CN)₂]Br (κ -Br salt), and κ -(BEDT-TTF)₂Cu(NCS)₂ (κ -NCS salt). We observed the reduction of $1/T_1T$ starting at the temperature higher than T_c in κ -Br salt. Microscopic observation of the quasiparticle density of states in the fluctuating SC state revealed the effects of short-range Cooper pairs induced in the normal state to the quasiparticle density of states. We also performed systematic measurements in the fields both parallel and perpendicular to the conduction plane in κ -Br and κ -NCS salts, and confirmed that the reduction of $1/T_1T$ above T_c is observed only in κ -Br salt regardless of the external field orientation.

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I. INTRODUCTION

Near the second order phase transition, thermal and quantum fluctuations induce a short-range coherence even above the transition temperature. The universality of physical quantities in this critical regime has been intensively studied for various types of magnetic transitions [1]. For the second-order superconducting (SC) transition, the short-range coherence of SC order parameter should also be induced in the normal state, where the thermal average of order parameter does not possess the finite value. The anomaly accompanied with fluctuating SC order parameter should be investigated to proceed universal understanding of the second-order phase transition. The prominent effect of fluctuating SC order parameter was observed by the Nernst effect measurement on cuprate superconductor [2], in which a vortexlike signal was detected in the critical regime above the SC transition temperature T_c . To reveal the mechanism for the fluctuating SC order parameter to affect the bulk properties, both theoretical and experimental studies have been carried out on the high- T_c cuprate superconductors [3–6]. However, enhanced magnetic fluctuations, which originate from the antiferromagnetic transition near the SC phase, contaminate the pure effect of fluctuating SC order parameter. In order to investigate the critical fluctuation of SC order parameter, we should examine a superconductor that shows SC transition in the conventional Fermi liquid state.

The observation of vortexlike signal by Nernst effect measurement in an organic superconductor κ -(BEDT-TTF)₂Cu[N(CN)₂]Br (BEDT-TTF: bis(ethylenedithio)tetrathiafulvalene) leads us to study the fluctuating SC state in a series of κ -(BEDT-TTF)₂X salts [7], because in the organic superconductors the conventional Fermi liquid state is established when superconductivity sets in. Besides, the effects associated with superconductivity can be controlled by magnetic fields, as the upper critical field $B_{c2}^{\perp} \simeq 10$ T is accessible with conventional SC magnets [8,9]. The precursor of SC transition above T_c was detected also by magnetic torque, and magnetization measurements [10–12]. These experiments probed the vortices generated

by the short-range Cooper pairs in the normal state, and confirmed that fluctuating SC state is realized in κ -(BEDT-TTF)₂Cu[N(CN)₂]Br salt. Since the fluctuating SC state has been established, we should explore the variation of quasiparticle density of states (DOS) caused by the fluctuating SC order parameter, which is essential for the microscopic understanding of critical SC fluctuation [13], but cannot be observed by the bulk measurements because of the large magnetization from vortices.

The NMR spectroscopy enables us to measure directly the quasiparticle DOS when the system is in the Fermi liquid state. The previous nuclear spin-lattice relaxation rate $1/T_1$ measurement on cuprate superconductors could not observe separately the effect of SC fluctuations [4,5], because the strong spin fluctuations near antiferromagnetic phase violate the conventional Fermi liquid state. In the organic superconductors, as the spin fluctuations are weak enough to stabilize the Fermi liquid state above T_c , NMR experiment should be performed on κ -(BEDT-TTF)₂X salts.

The κ -(BEDT-TTF)₂X family salts are quasi-two-dimensional conductors. When $X = \text{Cu(NCS)}_2$ (κ -NCS salt), superconductivity is observed below $T_c = 9.4$ K [14], and when $X = \text{Cu[N(CN)}_2\text{]Cl}$, antiferromagnetic transition occurs at $T_N = 22$ K [15]. Another superconducting salt with $X = \text{Cu[N(CN)}_2\text{]Br}$ (κ -Br salt) is located very close to the antiferromagnetic phase, but the typical Fermi liquid behavior, namely temperature independent bulk susceptibility and T^2 dependence of resistivity, was clearly observed below 20 K [16,17]. The deuteration to κ -Br salt brings the electronic state toward the antiferromagnetic phase, and enhanced spin fluctuations in the deuterated κ -Br salt violates the Fermi liquid state [18]. The deuterated salts are referred to as κ -d[n,n]-Br ($n = 0 \sim 4$) depending on the numbers of substituted hydrogen at each ethylene group of BEDT-TTF molecule. The ¹³C NMR experiment on κ -d[4,4]-Br salt observed the reduction of $1/T_1T$ much above T_c [19]. This anomalous reduction of $1/T_1T$ can be interpreted by either magnetic or SC fluctuations, just as in the case for cuprate superconductors. Therefore, we measured $1/T_1T$ on nondeuterated κ -d[0,0]-Br and κ -NCS salts, which demonstrate the Fermi liquid state at T_c , and investigated the pure effect of fluctuation SC

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order parameter. The Nernst effect measurements detected the vortexlike signal above T_c in κ -Br salt, and no such signal in κ -NCS salt [7]. The X anion dependence of SC criticality was interpreted as the difference in the proximity to antiferromagnetic phase. Nam *et al.* proposed that fluctuation in the phase of SC order parameter would be induced when the quasiparticles are nearly localized in the vicinity of antiferromagnetic insulator phase. On the other hand, magnetic torque measurements concluded that comparable SC fluctuation effect was observed in κ -Br and κ -NCS salts [12,20]. This inconsistency can be due to the difference in the external field direction. The external field was applied perpendicular to the conduction plane for the Nernst effect measurement, whereas parallel to the conduction plane for the magnetic torque measurement. As the experimental constraint determines the field orientation for these techniques, other experiments that can be conducted in both parallel and perpendicular fields are required. In the present ^{13}C NMR experiment on κ -Br and κ -NCS salts, we measured $1/T_1T$ in the magnetic field both parallel and perpendicular to the conduction plane.

II. EXPERIMENTAL

The single-crystal κ -Br and κ -NCS salts were grown using electrochemical reaction. The typical dimension is $1.9 \times 1.5 \times 0.6 \text{ mm}^3$. We utilized the ^{13}C enriched BEDT-TTF molecule, for which single side of the central $\text{C}=\text{C}$ bond was enriched with ^{13}C [21]. This asymmetric molecule eliminates the NMR peak splitting due to the nuclear spin-spin coupling at the $\text{C}=\text{C}$ bond (Pake doublet) [22]. We determined the mean-field T_c of our samples from magnetization measurement at low field as $T_c = 11.4 \text{ K}$ for κ -Br, $T_c = 9.3 \text{ K}$ for κ -NCS, which are consistent with the previous studies, and evidence the high quality of our samples.

The conventional saturation-recovery method was employed for the $1/T_1$ measurement. For κ -(BEDT-TTF) $_2X$ salt, when the field is along the c axis, two crystallographically independent ^{13}C sites give rise to two NMR peaks, which are labeled as inner and outer sites [23]. At high temperatures, these two peaks can be clearly resolved, as shown in the inset of Fig. 1, and the relaxation time T_1 can separately be determined. As the result, the inner site is found to have three times longer T_1 than that for the outer site. This ratio is temperature independent, because the difference in T_1 is determined by the site-dependent, and temperature-independent hyperfine coupling constants. At low temperatures, as these peaks are not resolved due to line broadening, and the reduction of Knight shift, we integrated the whole spectrum and fitted the obtained recovery curve with two component exponential function,

$$\frac{M_0 - M(t)}{M_0} = 0.5 \exp\left(\frac{-t}{T_1^{\text{outer}}}\right) + 0.5 \exp\left(\frac{-t}{T_1^{\text{inner}}}\right).$$

We fixed the ratio $T_1^{\text{inner}}/T_1^{\text{outer}} = 3$. As shown in Fig. 1, all the recovery curves, including the temperatures and fields above and below the SC transition, are sufficiently fitted with this function, which is represented by a dashed line. The recovery of nuclear magnetization shows a universal behavior, when the horizontal axis is scaled by T_1^{inner} determined at each temperature. This scaling by T_1 indicates that the obtained T_1

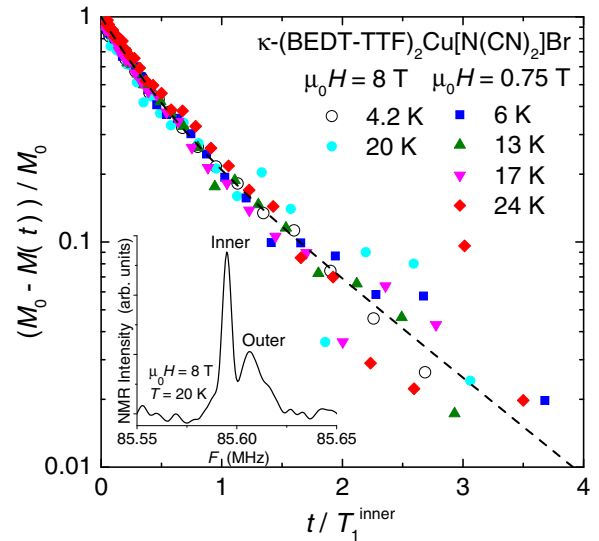


FIG. 1. (Color online) Recovery profile of nuclear magnetization obtained in wide range of temperatures and magnetic fields. The horizontal axis was scaled by T_1^{inner} determined at each temperature. The universal behavior was observed both in the SC and normal states, which confirms that the obtained T_1 reflects intrinsic character of quasiparticle density of states. Inset shows a typical ^{13}C NMR spectrum in field along c direction. At high temperature, two peaks labeled as inner and outer sites were observed. These peaks were superimposed at low temperature due to line broadening and reduction of Knight shift.

characterize correctly the time scale for nuclear magnetization to relax, regardless of the fitting procedures.

We also performed NMR experiments on deuterated κ - $d[n,n]$ -Br salts ($n = 2, 4$). For the deuterated samples, field orientation was fixed to the c direction to eliminate the angle dependence of $1/T_1T$ values originating from the angle dependent hyperfine coupling constant and investigated quantitatively the deuteration effect.

III. RESULTS AND DISCUSSIONS

Figure 2 shows the temperature dependence of $1/T_1T$ for κ -Br salt in various magnetic fields. The temperature-independent Fermi liquid behavior was observed below 20 K, which confirms that the magnetic fluctuations near the antiferromagnetic transition are sufficiently suppressed, and the Fermi liquid state is established when superconductivity sets in. In the Fermi liquid state, $1/T_1T$ is proportional to the square of the DOS at the Fermi energy $N(E_F)$,

$$\frac{1}{T_1T} = \frac{\pi k_B}{\hbar} A_{\text{hf}}^2(\theta) N^2(E_F). \quad (1)$$

Here, $A_{\text{hf}}(\theta)$ is the angle dependent hyperfine coupling constant. This Korringa relation is modified either by enhanced magnetic fluctuations near magnetic transition, or by the SC fluctuation near T_c , which corrects the quasiparticle DOS [4,24]. The vertical dashed line in Fig. 2 denotes the mean-field T_c at 0.75 T [$T_c(0.75 \text{ T}) = 10 \text{ K}$], which was determined by the abrupt decrease in NMR shift at 0.75 T [right scale of Fig. 2(a)]. When the magnetic field of 8 T is

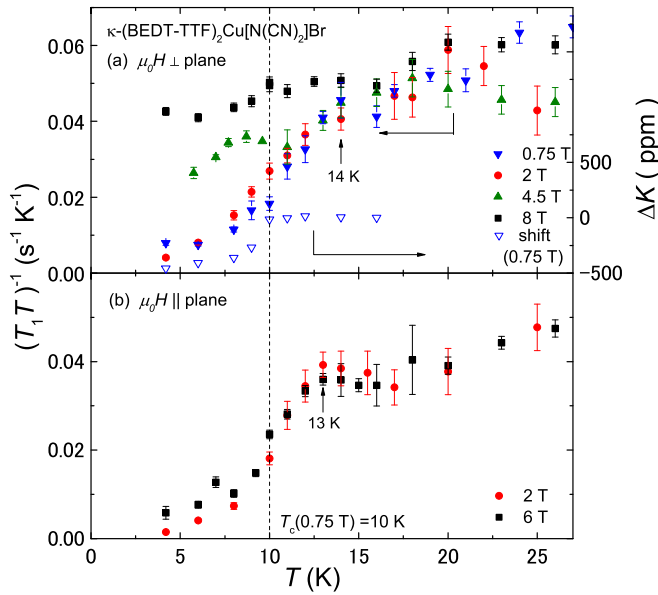


FIG. 2. (Color online) Temperature dependence of $1/T_1T$ for κ -Br salt in various magnetic fields perpendicular (a) and parallel (b) to the conduction plane. Open symbol shows the temperature dependence of NMR shift in 0.75 T. Dashed line denotes the mean-field $T_c = 10$ K, which was determined by the abrupt decrease in NMR shift. The reduction of $1/T_1T$ observed above T_c indicates that the fluctuating SC order parameter affects the quasiparticle DOS.

applied perpendicular to the conduction plane H_\perp [Fig. 2(a)], superconductivity is completely destroyed and Fermi liquid behavior persists down to 4.2 K. In smaller fields, $1/T_1T$ deviates from the Fermi liquid behavior below 14 K, which is higher than the mean-field T_c of 10 K. We suggest that the decrease in $1/T_1T$ above T_c is caused by the fluctuating SC order parameter.

The reduction of $1/T_1T$ was also observed in the parallel magnetic field [Fig. 2(b)]. As 6 T is not strong enough to suppress superconductivity and induce Fermi liquid behavior at low temperatures, the onset of $1/T_1T$ reduction was determined as the temperature at which $1/T_1T$ deviates from the high-temperature Fermi liquid behavior. The onset for H_\perp (14 K) is slightly higher than that for H_\parallel (13 K). This subtle difference is due to the anisotropy of coherence length. Since decrease in $1/T_1T$ at temperatures higher than T_c was observed in both H_\perp and H_\parallel , we conclude that κ -Br salt shows a fluctuating SC state regardless of the magnetic field directions. Theoretical study has revealed that SC fluctuations can correct quasiparticle DOS in three different processes, which are called Aslamazov-Larkin (AL), Maki-Tompson (MT), and DOS processes [3]. The AL process is irrelevant to the dynamical susceptibility, which determines $1/T_1T$. Present results indicate that the DOS process, which reduces the quasiparticle DOS, is dominant in κ -Br salt compared to the MT process, which increases $1/T_1T$.

The same measurements were performed for κ -NCS salt, and the results were displayed in Fig. 3. The Fermi liquid behavior was observed at all temperature regions in $H_\perp = 8$ T. At a small field, deviation of $1/T_1T$ from the Fermi liquid behavior starts almost at the mean-field T_c at 2 T [$T_c(2\text{ T}) = 9$ K].

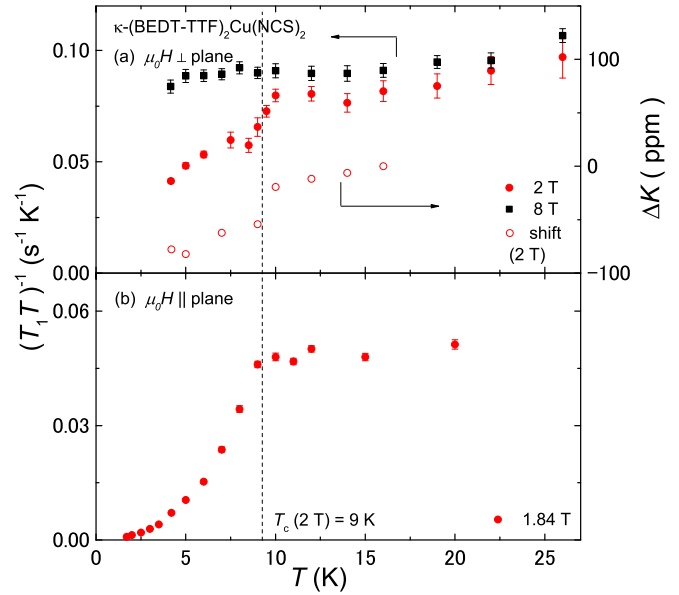


FIG. 3. (Color online) Temperature dependence of $1/T_1T$ for κ -NCS salt in magnetic fields perpendicular (a) and parallel (b) to the conduction plane. Open symbol shows the temperature dependence of NMR shift in 2 T, which determined the mean-field $T_c = 9$ K. Although T_c is comparable to that for κ -Br salt, κ -NCS salt shows the reduction of $1/T_1T$ above T_c only in the temperature range very close to T_c .

9 K]. Similarly, in a parallel field, the decrease in $1/T_1T$ from the temperature-independent value was observed only below T_c . These results indicate that the temperature region, where SC fluctuations become significant, is limited very close to T_c in κ -NCS salt.

Now, we compare the results of κ -Br and κ -NCS salts. Although SC transition occurs at comparable temperatures in both salts, the reduction of $1/T_1T$ due to the SC fluctuation was observed only in κ -Br salt, consistent with Nernst effect and magnetization measurements [7,11]. The SC parameters for κ -Br and κ -NCS salts should be compared to understand the universal behavior of the fluctuating SC state.

In the critical regime above T_c , the short-range SC coherence can be observed when the thermal energy becomes comparable to the energy cost required to induce SC gap within the Pippard length ξ . Therefore, the critical temperature range is determined by the SC gap size Δ , T_c , and ξ , as

$$\frac{|T - T_c|}{T_c} \equiv G \propto \left(\frac{k_B T_c}{\xi_\parallel^2 \xi_\perp \Delta} \right)^2, \quad (2)$$

where ξ_\parallel and ξ_\perp are the in-plane and interplane Pippard length. The experimentally determined Pippard lengths are $\xi_\parallel = 3.7$ nm and $\xi_\perp = 0.6$ nm for κ -Br, and $\xi_\parallel = 7.0$ nm and $\xi_\perp = 0.5$ nm for κ -NCS [25]. The typical temperature range for a three-dimensional BCS superconductor is as narrow as $G \sim 10^{-6}$. Wider critical regime is expected for low dimensional superconductors with short ξ_\perp . Our experimental results suggest that G of κ -Br salt reaches to the order of 10^{-1} , which is comparable to the results obtained for high- T_c cuprate.

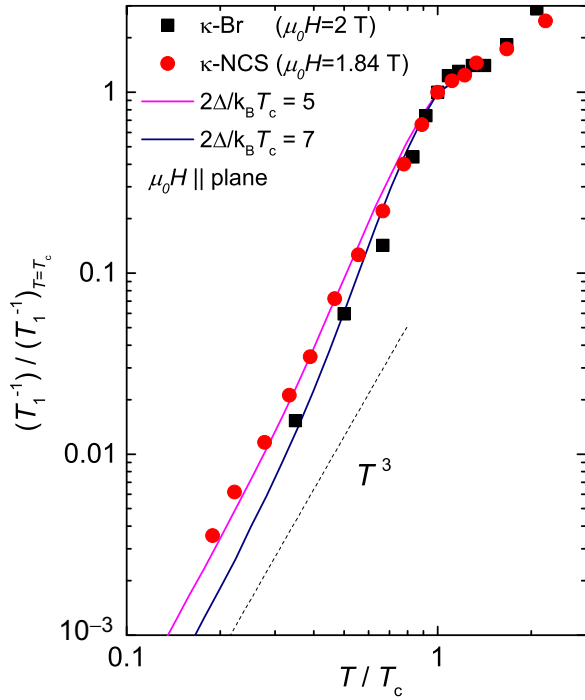


FIG. 4. (Color online) SC parameter $2\Delta/k_B T_c$ estimated from the temperature dependence of $1/T_1$ in the SC state. The vertical axis is $1/T_1$ scaled by the value at T_c , and the horizontal axis is the reduced temperature T/T_c . We estimated $2\Delta/k_B T_c$ by fitting the experimental data to the theoretical curve for the d -wave superconductor.

We estimated the ratio $2\Delta/k_B T_c$ from the temperature dependence of $1/T_1$ in the SC state. Figure 4 shows the temperature dependence of $1/T_1$ normalized at T_c for κ -Br and κ -NCS salts. The power-law temperature dependence suggests that d -wave superconductivity with nodes on the SC gap is realized in both κ -Br and κ -NCS salts. The fit to the temperature dependence with the theoretical curve for d -wave superconductivity gives the estimation of $2\Delta/k_B T_c$, which is 7 for κ -Br salt and 5 for κ -NCS salt. The ratio between κ -Br and κ -NCS salts is in perfect agreement with the values reported in the literature [25]. We note that the large Δ for κ -Br salt seems to reduce the critical temperature regime defined in Eq. (2). However, because the Pippard length is also related to Δ as $\xi = \hbar v_F / \pi \Delta$, the larger Δ increases the critical regime by reducing the coherence length. Here we assumed that only the coherence length in the conduction plane ξ_{\parallel} is determined by Δ because of the two-dimensional nature of superconductivity in κ salts. In fact, ξ_{\parallel} for κ -Br salt is twice shorter than that for κ -NCS salt, whereas ξ_{\perp} is almost comparable between κ -Br and κ -NCS salts [25].

The larger Δ is expected for the deuterated κ - d [4,4]-Br salt, which is located very close to the antiferromagnetic phase. A previous NMR study for κ - d [4,4]-Br salt suggested a possibility that the critical SC regime starts from rather high temperatures [19]. We also measured $1/T_1 T$ near T_c for κ - d [n,n]-Br salts with $n = 0, 2, 4$ applying the magnetic field of 6 T along the c direction. In Fig. 5, a strong temperature dependence of $1/T_1 T$ was observed around 20 K in κ - d [4,4]-Br salt, consistent with the previous report [19].

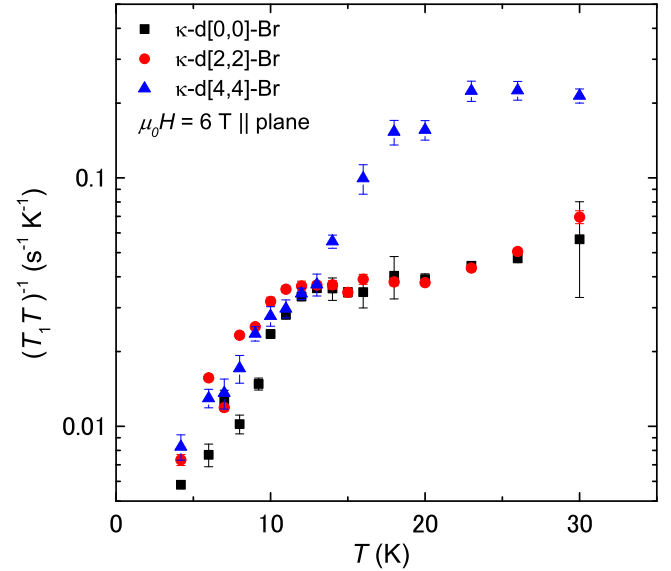


FIG. 5. (Color online) Deuterium effect on the FL state near T_c . Strong temperature dependence due to the reduction of spin term was observed in κ - d [4,4]-Br salt, while κ - d [0,0]-Br and κ - d [2,2]-Br salts show the FL liquid behavior below 20 K. In κ - d [4,4]-Br, the effects of the SC fluctuation were contaminated by the strong magnetic fluctuations near the antiferromagnetic phase transition.

This behavior cannot be directly interpreted as the effect of fluctuating SC order parameter, because enhanced magnetic fluctuations contaminate the pure effect of SC fluctuations. In the vicinity of antiferromagnetic phase transition, the observed $1/T_1 T$ is the sum of the contributions from weakly correlated Fermi surface (FL term) and strongly nested Fermi surface at the ordering vector \mathbf{Q} (spin term),

$$\frac{1}{T_1 T} = \left(\frac{1}{T_1 T} \right)_{\text{FL}} + \left(\frac{1}{T_1 T} \right)_{\text{spin}}. \quad (3)$$

The strong temperature dependence observed in κ - d [4,4]-Br salt indicates that the spin term remains dominant until low temperatures. The increase in $1/T_1 T$ by enhanced magnetic fluctuations was observed only above 30 K in κ - d [0,0]-Br and κ - d [2,2]-Br salts. This spin term is suppressed below 20 K, and the Fermi liquid state is stabilized at T_c in these salts. The comparable constant value of $1/T_1 T = 0.035 \text{ s}^{-1} \text{ K}^{-1}$ indicates that the deuterium does not significantly modify the FL term. We suggest, from the deuterium independent behavior of $1/T_1 T$ below 14 K, that κ - d [4,4]-Br salt also shows the reduction of FL term due to SC fluctuation near T_c , although details were hindered by the spin term.

IV. CONCLUSION

In conclusion, we observed the reduction of $1/T_1 T$ starting above T_c in κ -Br salt in fields both parallel and perpendicular to the conduction plane, and addressed the fluctuating SC order parameter as the origin of this reduction. The microscopic NMR experiment enabled the direct observation of quasiparticle DOS in the fluctuating SC state. We revealed that, in the fluctuating SC state in κ -Br salt, the quasiparticle

DOS is reduced from the normal-state value because of the dominant DOS process. In κ -NCS salt, the reduction of quasiparticle DOS due to SC fluctuation was observed only in the temperature range very close to T_c . Our systematic study clarified the field-orientation dependence of the SC fluctuation and convinced that the SC fluctuation has a larger effect on $1/T_1T$ in κ -Br salt than in κ -NCS salt. From the estimation of SC gap size for κ -Br and κ -NCS salts, we suggest that the small critical regime in κ -NCS salt is due to the long coherence length. We also measured $1/T_1T$ in the deuterated κ - $d[n,n]$ -Br salts and found that the deuteration induces the large spin term even at T_c , which contaminates

the pure effect of SC fluctuation. These results indicate that κ - $d[0,0]$ -Br salt is an ideal system to study the pure effect of SC fluctuation and provide microscopic information to understand the electronic properties in the fluctuating SC state.

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