Quantum critical behavior in superconducting $Na_x(H_3O)_zCoO_2 \cdot yH_2O$ observed in a high-field Co NMR experiment

Y. Ihara,[1,*] H. Takeya,[1] K. Ishida,[1,2,†] C. Michioka,[3] K. Yoshimura,[3] K. Takada,[4] T. Sasaki,[4] H. Sakurai,[5] and E. Takayama-Muromachi[5]

[1]*Department of Physics, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan*
[2]*International Innovation Center, Kyoto University, Kyoto 606-8501, Japan*
[3]*Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan*
[4]*Nanoscale Materials Center, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan*
[5]*Advanced Nano Materials Laboratory, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan*

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Co nuclear magnetic resonance (NMR) measurements are performed on superconducting $Na_x(H_3O)_zCoO_2 \cdot yH_2O$ with a bilayered hydrate structure. External fields are applied exactly parallel to the CoO_2 plane on a high-quality powdered sample, which is aligned in a strong magnetic field. When superconductivity is suppressed by external magnetic fields, the nuclear spin-lattice relaxation rate divided by temperature $(1/T_1T)$ continues to increase down to $T_c(H)$, which is the superconducting transition temperature under a magnetic field H. From the analyses of the temperature variation, it was found that a sample with $T_c \sim 4.8$ K, which is the maximum T_c, possesses magnetic fluctuations with a quantum critical character. This suggests the intimate relationship between superconductivity and quantum critical fluctuations in the hydrate cobaltate. We determined $T_c(H)$ and constructed the $H_{c2}-T_c$ phase diagram from the present NMR measurements. The field dependence of $T_c(H)$ is discussed.

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Superconductivity realized near magnetism has attracted great interest of researchers studying condensed matter physics, because superconducting mechanisms other than the conventional electron-phonon interaction have been considered to work in such superconductors. Although several kinds of unconventional superconductors in the strongly correlated electron systems have been discovered near a magnetic phase and have been intensively investigated,[1] the relationship between superconductivity and magnetism has not been fully understood.

In the newly discovered hydrate-cobaltate superconductor $Na_x(H_3O)_zCoO_2 \cdot yH_2O$,[2] magnetic ordering was observed in the bilayered hydrate (BLH) cobaltate from nuclear quadrupole resonance (NQR), muon spin rotation, and susceptibility measurements.[3–5] In our previous paper, we developed a phase diagram of BLH $Na_x(H_3O)_zCoO_2 \cdot yH_2O$ on the basis of the Co-NQR measurements on 12 samples with a variety of superconducting (SC) (T_c) and magnetic (T_M) transition temperatures,[6] suggesting that superconductivity in the hydrate-cobaltate system is also related to magnetism. In the phase diagram, the Co-NQR frequency ν_Q was used as a tuning parameter of the system. It seems that superconductivity with the maximum T_c of the system is realized when the magnetic transition temperature T_M goes down to zero, i.e., magnetic fluctuations possess a quantum critical character.

In this Brief Report, we report the temperature variation of nuclear spin-lattice relaxation rate divided by temperature $1/T_1T$ in the sample with $T_c \sim 4.8$ K, when superconductivity is suppressed by strong magnetic fields. From this measurement, we could know the properties of magnetic fluctuations hindered by the occurrence of superconductivity. We found that $1/T_1T$ continues to increase in the field-induced normal state, and showed that the magnetic fluctuations possess a quantum critical character from the analyses of temperature dependence of $1/T_1T$ down to 1.5 K. This result also strongly suggests that superconductivity with the maximum T_c is related to quantum critical fluctuations.

In order to investigate magnetic fluctuations inherent to superconductivity, we employed a high-quality powdered sample.[3] T_c of our sample is as high as 4.8 K, which is the highest within the cobaltate superconductors we have ever measured. During the measurement, we have kept the sample frozen to maintain sample quality, because water molecules in the compound easily evaporate into the air under an ambient condition. From the relation between T_c and NQR frequency in our phase diagram, the sample was found to be located at the optimum condition for the superconductivity.

The powdered sample was mixed with nonreactive liquid "Fluorinert." This sample was aligned in 8 T and was fixed by solidifying the mixture below 250 K. Because of the anisotropy of the susceptibility, the crystalline c axis was oriented perpendicular to the magnetic-field direction.[7] Therefore, the external field is randomly applied within the CoO_2 plane, and exactly perpendicular to the c axis.

The NMR spectrum in Fig. 1 is consistently explained by a typical two-dimensional powder pattern.[8] The external field is randomly applied within the plane perpendicular to the principal axis of the electric field gradient (EFG) (c axis in this compound). The dotted line displayed in Fig. 1 is the simulated NMR spectrum calculated on the above condition. Most of the spectral peaks, except for the sharp peak marked with an asterisk, were accounted for by the calculation. We assigned the peak marked with the asterisk as the signal from an impurity phase, because the signal has no angle dependence and a long T_1. The signal intensity from an impurity phase is too small to affect the central-peak measurement. The resonance peaks arising from ^{23}Na of the sample and

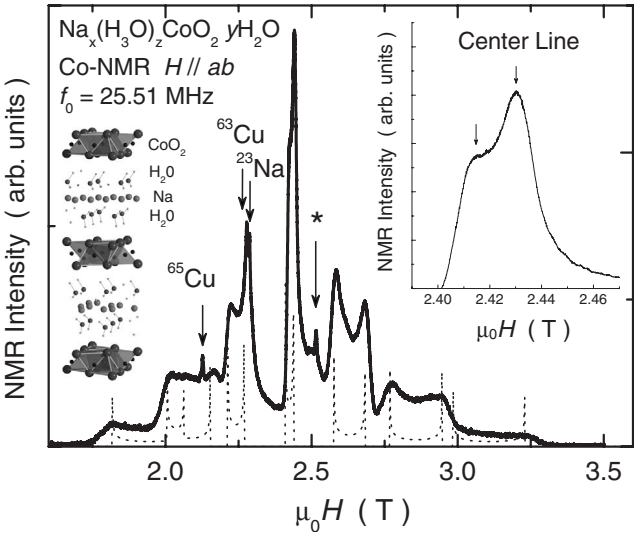

FIG. 1. Co-NMR spectrum with external field applied perpendicular to the c axis. The solid line and dotted line are the experimental result and simulated result, respectively. All the experimental results are reproduced by the simulation. The sharp peaks arising from ^{63}Cu and ^{65}Cu in the coil and ^{23}Na in the sample are observed, which are marked by arrows. The peak marked by an asterisk is the impurity phase (see in text). The inset is the close view of the central peak ($m=1/2 \leftrightarrow -1/2$ transition). A two-peak structure is observed.

from ^{63}Cu and ^{65}Cu of NMR coil were also observed, but were well separated from the central peak.

In this Brief Report, we concentrate on the central peak arising from the $m=1/2 \leftrightarrow -1/2$ transition, which is shown in the inset of Fig. 1. We found that the central peak consists of two peaks pointed by arrows.[9] The double-peak structure is ascribed to the in-plane anisotropy of the EFG and Knight shift. NMR spectra obtained in various fields above and below T_c are shown in Fig. 2, where the peak positions at $T > T_c$ are shown by arrows. Within the second-order perturbation of the electric quadrupole interaction against the Zeeman interaction, the difference of the magnetic fields (ΔH) between double central peaks at the resonant frequency of ν_0 is expressed as

$$\gamma_N \Delta H = (K_x - K_y)\nu_0 + A\frac{V_{zz}(V_{xx} - V_{yy})}{(1+K)\nu_0},$$

where K_α and $V_{\alpha\alpha}$ ($\alpha = x, y, z$) are Knight shift and EFG along the α direction, respectively, and γ_N is the nuclear gyromagnetic ratio. It should be noted that the resonant frequency (ν_0) dependence of the first term, which originates from Knight shift anisotropy, is opposite to the second term which represents the second-order effect of EFG. With increasing field, the difference of the magnetic fields becomes minimum around 4 T, and it becomes larger again above 7 T. The minimum of the splitting width was observed around 4 T, because the energy of the quadrupole interaction is comparable to that of the Zeeman interaction around this field.

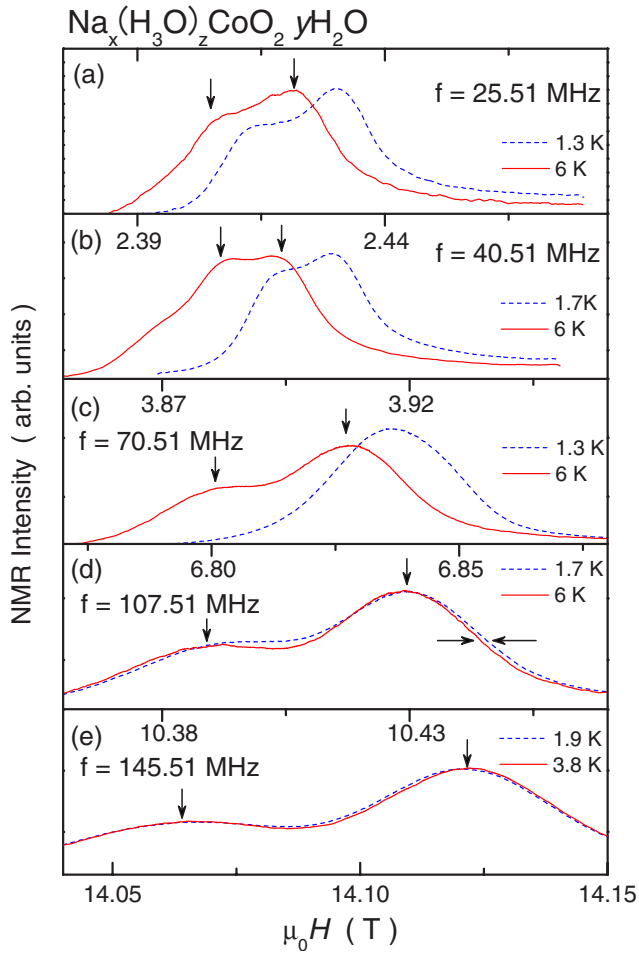

FIG. 2. (Color online) Field dependence of the central peak above and below $T_c(H)$. (a), (b), (c), (d), and (e) are measured around 2.5, 4, 7, 10, and 14 T. Solid lines and dotted lines of each figure are NMR spectra obtained above and below T_c, respectively. Peak positions which are determined by fitting the data by two component Gaussian are indicated by down arrows.

The in-plane anisotropy of Knight shift originates from two inequivalent directions in the CoO_2 layer, i.e., the Co-Co direction and Co-O direction. Taking into account the result obtained from the ^{17}O-NMR measurement,[10] strong temperature dependence of $1/T_1T$, which shows enhancement below 100 K, arises from magnetic correlations by way of the Co-O-Co coupling, because the same temperature dependence as $1/T_1T$ at the Co site was observed at the O site. This is consistent with the band calculation,[11] which suggests that the Co-Co direct coupling is weaker than the Co-O-Co coupling. We have also suggested from the Co-NQR measurements on SC and non-SC cobaltates[6] that the magnetic fluctuations which develop below 100 K might originate from e_g' band, forming six small holelike Fermi surfaces around K point. This is because the enhancement of $1/T_1T$ below 100 K was observed only in the BLH cobaltate, whose CoO_2 layer is compressed due to the water intercalation. The trigonal distortion of the CoO_2 layer is favorable for the appearance of the e_g' Fermi surface. Therefore, we consider that the strong magnetic fluctuations enhanced at low temperatures

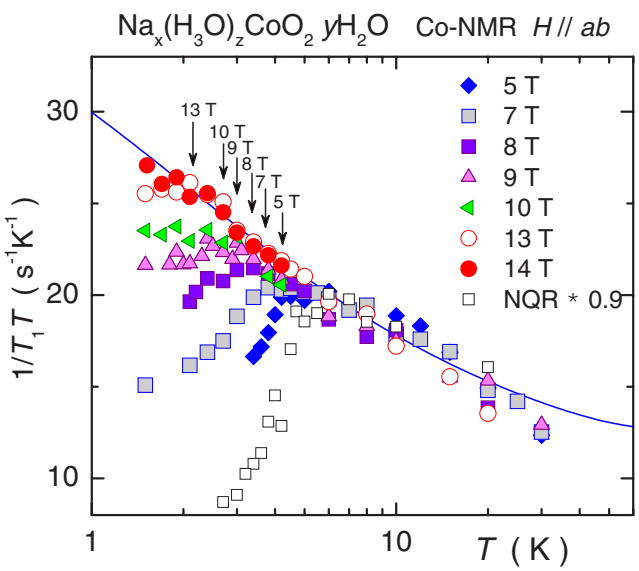

FIG. 3. (Color online) The temperature dependence of $1/T_1T$ at various magnetic fields. The symbol for each magnetic field is displayed in the figure. The red solid curve is the fitting function described in the text. The arrows indicate $T_c(H)$, at which $1/T_1T$ deviates from the normal-state temperature variation.

are related to the electron-electron correlation along the Co-O direction, which is consistent with the predominance of the e_g' band character.

$1/T_1T$ measured in various strengths of magnetic fields applied perpendicular to the c axis is shown in Fig. 3. T_1 was measured at the left side peak of the NMR spectra in Fig. 2. Above 5 K, the temperature variation of $1/T_1T$ is independent of external magnetic fields. In the previous paper,[6] we reported that the temperature dependence of $1/T_1T$ obtained with the Co-NQR measurement can be consistently fitted by a function with two fitting parameters a and θ, which is expressed as

$$\frac{1}{T_1T} = \left(\frac{1}{T_1T}\right)_{\mathrm{PG}} + \frac{a}{\sqrt{T-\theta}}. \tag{1}$$

The first term $(1/T_1T)_{\mathrm{PG}}$ is expressed as

$$\left(\frac{1}{T_1T}\right)_{\mathrm{PG}} = 8.75 + 15\exp\left(-\frac{250}{T}\right) \quad (\mathrm{s}^{-1}\,\mathrm{K}^{-1}),$$

which exhibits a pseudogap behavior above 100 K. Here, a is a proportionality constant related to the band structure at the Fermi level and to the hyperfine coupling constant, and θ is the ordering temperature in a magnetically ordered compound and is the measure of the closeness to the magnetic instability in the SC compound. The pseudogap behavior was commonly observed in monolayered hydrate and nonhydrate cobaltates[12] as in BLH compounds, while the additional second term expressed as $a/\sqrt{T-\theta}$ was observed only in BLH compounds.

Based on the framework of the self-consistent renormalization theory, the functional form of the second term is expected when magnetic fluctuations possess three-dimensional antiferromagnetic fluctuations.[13] In the measurements on the sample with $T_c \sim 4.8$ K under magnetic fields along the CoO_2 plane, the best fitting parameters are $a=30$ and $\theta=-1$ K, respectively, whereas these parameters were $a=20$ and $\theta=-1$ K in the NQR measurements. The difference of a is due to the anisotropy of $1/T_1T$; the NQR measures $1/T_1T$ along the c axis because the principal axis of the EFG is the c axis, while NMR in fields along the CoO_2 plane measures $1/T_1T$ perpendicular to the c axis. However, the identical value of θ between NQR and NMR measurements indicates that the magnetic fluctuations might be isotropic.

As shown in Fig. 3, $1/T_1T$ increases with decreasing temperature in the normal state, and the increase is interrupted by the occurrence of superconductivity. It is noteworthy that $1/T_1T$ continues to increase in the field-induced normal state and follows the fitting curve defined above 5 K. This is a great contrast to the Fermi-liquid (T_1T=constant) behavior. The continuous increase of $1/T_1T$ indicates that magnetic fluctuations continue to be enhanced down to $T_c(H)$ without showing the Fermi-liquid behavior. This non-Fermi-liquid behavior, which is understood through Eq. (1) with $\theta=-1$ K, strongly suggests that magnetic fluctuations possess the quantum critical character. This behavior is reminiscent of the specific-heat results on $CeCu_2Si_2$ (Ref. 14) and $CeCoIn_5$ (Ref. 15) in magnetic fields, both of which are situated at or near the quantum critical point.

When external fields are smaller than 7 T, $1/T_1T$ clearly decreases below T_c due to the opening of the SC gap. With increasing fields, the anomaly becomes broader, and $1/T_1T$ does not decrease but levels off below $T_c(H)$ in fields above 9 T. We determined $T_c(H)$ as the temperature below which $1/T_1T$ deviates from the temperature variation in the normal state. We could also identify $T_c(H)$ from the shift of the resonant fields, because the in-plane spin susceptibility decreases below T_c.[10,16–18] As shown in Figs. 2(a)–2(c), it was found that NMR spectra shift to the higher field below $T_c(H)$ in fields smaller than 7 T, due to the decrease of spin susceptibility in the SC state. At 10 T, the shift of a spectral maximum is hardly detectable, but a small change of the spectral shape, which is related to the decrease of spin susceptibility, was observed. This is indicated by horizontal arrows in Fig. 2(d) at the slope of the spectrum. In fields higher than 10 T, the decrease of spin susceptibility is subtle because superconductivity is almost destroyed by external fields. In contrast, the spectral width, which is related to the experimental accuracy of Knight shift, becomes broad in strong magnetic fields. As a result, the spectral shift accompanied by the occurrence of superconductivity becomes unclear at the broad peak, but slightly observable at the steep edge. When the external field is 13 T, the occurrence of superconductivity around 2.2 K was detected from the behavior of $1/T_1T$, but it seems that superconductivity does not occur down to 1.9 K in 14 T from no obvious difference between the NMR spectra at 3.8 K and at 1.9 K and the behavior of $1/T_1T$, which are shown in Figs. 2(e) and 3, respectively. To confirm the superconductivity in high fields, determination of $T_c(H)$ using other experimental techniques is also required.

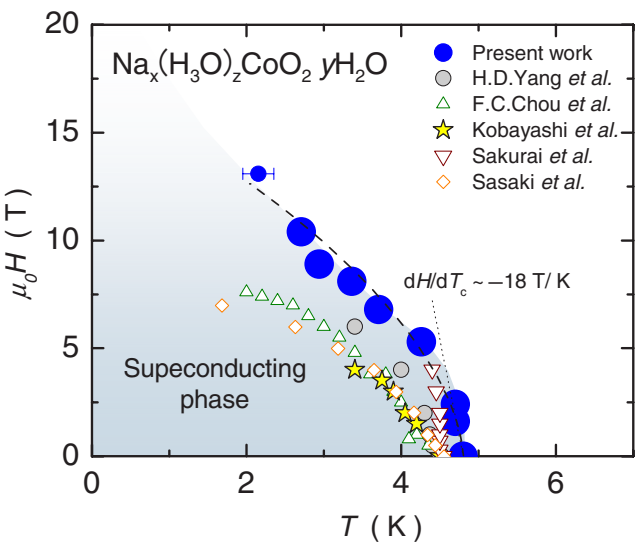

FIG. 4. (Color online) The field dependence of SC transition temperature $T_c(H)$. Larger circles in the present data are determined both from $1/T_1T$ and Knight shift measurements. The smaller circle is T_c at 13 T, which is determined only from the temperature dependence of $1/T_1T$. $T_c(H)$ of other groups(Refs. 7 and 19–22) are also shown for comparison.

Figure 4 displays the magnetic-field dependence of $T_c(H)$ when fields are applied exactly perpendicular to the c axis. $T_c(H)$ reported so far is also plotted for comparison.[7,19–22] The large circles of our data represent $T_c(H)$ identified from both $1/T_1T$ and Knight shift measurements, while the smaller circle at 13 T indicates $T_c(H)$ determined only from $1/T_1T$. As seen in Fig. 4, $T_c(H)$ shows very weak field dependence and the slope dH/dT_c below 3 T is as steep as −18 T/K. This estimation is in agreement with that reported in Ref. 19. We point out that the similar field independent behavior of $T_c(H)$ was observed in a quasi-two-dimensional (2D) organic superconductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br when fields are applied exactly parallel to the conducting plane.[23] This is because the orbital effect is suppressed due to the 2D character of the compounds. In the cobaltate superconductors, $T_c(H)$ gradually decreases by applying a magnetic field greater than 5 T, but the compound remains superconducting above at least 10 T, which is higher than the Pauli limiting field estimated using a simple equation $H_p = 1.85T_c = 8.8$ T. It is quite important to investigate the physical properties in $Na_x(H_3O)_zCoO_2 \cdot yH_2O$ in high fields above 13 T, because the realization of a novel SC state, such as Fulde-Ferrell-Larkin-Ovchinnikov state, or multiple SC phases might be suggested. NMR studies on a high-quality single crystal are highly desired.

In conclusion, from the high-field Co-NMR measurements on the aligned $Na_x(H_3O)_zCoO_2 \cdot yH_2O$ sample with $T_c \sim 4.8$K, we found that $1/T_1T$ continues to increase down to $T_c(H)$ when superconductivity is suppressed by magnetic fields. The temperature dependence of $1/T_1T$ in the field-induced normal state strongly suggests that magnetic fluctuations in the sample with the maximum T_c possess a quantum critical character. Taking into account the previous Co-NQR studies on samples, we strongly suggest that the superconductivity in the hydrate cobaltate is induced by the quantum critical fluctuations.

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*ihara@scphys.kyoto-u.ac.jp
†kishida@scphys.kyoto-u.ac.jp

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