Possible unconventional superconductivity in Na$_{x}$CoO$_2$$y$H$_2$O probed by $\mu$SR

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Abstract

The superconducting property of recently discovered sodium cobalt oxyhydrate, Na$_{0.35}$CoO$_2$1.3H$_2$O ($T_c = 4.5$ K), has been studied by means of muon spin rotation/relaxation ($\mu$SR) down to 2 K. It was found that the zero-field muon spin relaxation rate is independent of the temperature, indicating that no static magnetism appears in this compound, at least above 2 K. The result also provides evidence against the breakdown of time-reversal symmetry for the superconducting order parameter. Meanwhile, the muon Knight shift at 60 kOe shows no obvious reduction below $T_c$, suggesting that the local spin susceptibility is preserved upon a superconducting transition. Considering these observations, possible unconventional superconductivity of Na$_{0.35}$CoO$_2$1.3H$_2$O is discussed.

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The recent discovery of superconductivity in a novel cobalt oxide, \( \text{Na}_x \text{CoO}_2y \text{H}_2\text{O} \) \((x = 0.35, y = 1.3)\), with the transition temperature \( T_c \sim 5 \text{ K} \), is attracting much interest[1]. The compound has a lamellar structure consisting of \( \text{CoO}_2 \), \( \text{Na} \) and \( \text{H}_2\text{O} \) layers, where the two-dimensional (2D) \( \text{CoO}_2 \) layers are separated by thick insulating \( \text{Na} \) or \( \text{H}_2\text{O} \) layers. This structure is similar to high-\( T_c \) cuprate superconductors (HTSCs) in the sense that they also have a layered structure of 2D-CuO\(_2\) sheets separated by insulating layers. It is well established that \( \text{Cu}^{2+} (S = 1/2) \) atoms on a square lattice exhibit antiferromagnetic (AF) ordering in the parent compounds of HTSCs, where the superconductivity occurs when the AF state is suppressed by carrier doping. On the other hand, Co atoms form a 2D triangular lattice on the \( \text{CoO}_2 \) layers, where a strong magnetic frustration is anticipated. Thus, while \( \text{Na}_{0.35} \text{CoO}_21.3\text{H}_2\text{O} \) may be viewed as an electron-doped Mott insulator for a low-spin \( \text{Co}^{4+} (S = 1/2) \) with electron doping of \( x=35\% \), the electronic state may be considerably different from cuprates.

Although several experiments have revealed interesting properties of the present system[2, 3, 4, 5, 6, 7], the situation is far from reaching a consensus on the important issues, including that on the pairing symmetry of superconductivity. Meanwhile, based on the unique structure of the 2D-triangular Co lattice, many theoretical models predicting a variety of unconventional superconductivity have been proposed. For example, superconductivity with symmetries of the \( p + ip \) state[8], the \( d_{x^2-y^2} + id_{xy} \) state[9, 10, 11, 12], and the \( f \) state[13] are argued. It is notable that some of these states break the time-reversal symmetry of the Cooper pairs, leading to the appearance of a weak spontaneous internal magnetic field in accordance with the superconducting transition. Such an internal field can be detected with utmost sensitivity by the zero-field muon spin relaxation (ZF-\( \mu \)SR) technique.

Furthermore, the muon Knight shift give crucial information about the pairing symmetry of the Cooper pairs. Up to now, there are two \( ^{59}\text{Co-NMR} \) Knight shift measurements. Waki et al. reported a Knight shift that is independent of temperature through \( T_c \), which suggests a spin triplet state for the pairing symmetry[5]. On the other hand, Kobayashi et al. showed a decrease of the Knight shift with decreasing temperature[4]. The Knight shift results are presently a controversial issue. Thus, it is quite important to obtain more clues brought by other experimental techniques, including \( \mu \)SR, to settle the issue of paring symmetry. Since the muon has a spin of 1/2, one can deduce the muon Knight shift without any complication due to electric field gradient. This feature is an advantage of the muon Knight shift over
NMR at $^{59}$Co ($I = 7/2$) in which a complex signal pattern is observed.

In this letter, we report on the magnetic and superconducting properties of Na$_{0.35}$CoO$_2$1.3H$_2$O studied by means of the muon spin rotation/relaxation method ($\mu$SR) down to 2 K. It is inferred from the ZF-$\mu$SR measurement that there is no appreciable static magnetism over the entire temperature range across $T_c$, indicating that the time-reversal symmetry is preserved in the superconducting state. The muon Knight shift at 60 kOe is almost independent of the temperature irrespective of the superconducting transition, which suggests a spin triplet symmetry for the order parameter.

Powder specimens of Na$_{0.35}$CoO$_2$1.3H$_2$O, including a deuterated one (D$_2$O $\simeq$ 75 %), were synthesized, as described in Ref.[1]. Each specimen was characterized by measuring the magnetic susceptibility prior to a $\mu$SR measurement. Conventional $\mu$SR measurements under zero field and a weak transverse field ($TF, H = 374$ Oe) were carried out at the $\pi$A-port of the Meson Science Laboratory, High Energy Accelerator Research Organization (KEK). The muon Knight shift measurements ($TF-\mu$SR at 60 kOe) were performed on the M15 beamline of TRIUMF. In both cases, a positive muon beam with a momentum of 27 MeV/c was implanted to a powder specimen placed in a He-gas exchange cryostat, where special precaution was taken to cool down the specimen rapidly below $\sim$100 K to preserve its water content. For ZF-$\mu$SR, residual field was reduced to below 10 mOe by using three pairs of correction magnets. For a high-field measurement at 60 kOe, a powder specimen was secured with Apiezon-N grease to prevent an alignment of fine crystals in the specimen by a strong field.

Fig. 1 shows the time evolution of the muon spin polarization in Na$_{0.35}$CoO$_2$1.3H$_2$O at 10 K and 2 K under zero magnetic field. At 10 K, the muon spin depolarizes due to a static random local field, which originates from the $^{59}$Co, $^{23}$Na and $^1$H nuclear magnetic moments. These spectra can be described by the Kubo-Toyabe relaxation function, $G_{KT}(\Delta, \nu, t)[1]$, as indicated by the solid line in Fig.1. Here, $\Delta/\gamma_\mu$ is the second moment of the field distribution at the muon site, with $\gamma_\mu$ being the muon gyromagnetic ratio ($=2\pi \times 13.55$ kHz/Oe), and $\nu$ is a fluctuation rate of the nuclear dipolar field. From a fitting analysis, we obtained $\Delta/\gamma_\mu \sim 5.0$ G and $\nu \sim 0.22 \mu s^{-1}$ at 10 K. By comparing the experimental value of $\Delta$ in the normal phase (10 K) of Na$_{0.35}$CoO$_2$1.3H$_2$O($\Delta = 0.425(4)$ $\mu s^{-1}$) and that in the deuterated specimen ($\Delta = 0.243(3)$ $\mu s^{-1}$, also appears in Fig.1), together with calculated mapping of $\Delta$, the muon stopping site was identified near (0.2,0.25,0.12).
As evident in Fig. 1, we observed no significant change in the ZF-$\mu$SR time spectrum while the temperature passed $T_c$. Fig. 2 shows the temperature dependence of the dipolar width ($\Delta$), which is nearly independent of the temperature within an accuracy of 0.1 Oe. This result clearly demonstrates the absence of static magnetism over the time window of $\mu$SR ($10^{-9} \sim 10^{-5}$ s). The upper bound for the possible magnetic moment was estimated to be $0.001 \mu_B$/Co in Na$_{0.35}$CoO$_2$1.3H$_2$O by using the hyperfine coupling constant, $A_{hf} = -134$ Oe/$\mu_B$, which we derive later.

It is theoretically suggested that spontaneous magnetic fields are induced below the superconducting transition when the superconductivity is carried by the ‘magnetic’ Cooper pairs. For example, Wang et al. proposed that the system falls into a pairing state described by $d_{x^2-y^2} + id_{xy}$, and that the orbital current produces a spontaneous magnetic field, which is estimated to be 10-100 Oe [11]. Tanaka and Hu proposed a chiral $p$-wave state, which also breaks the time-reversal symmetry [8]. Such a spontaneous field has been observed in a spin-triplet superconductor, Sr$_2$RuO$_4$ [15, 16], and quite recently in a heavy fermion superconductor, PrOs$_4$Sb$_{12}$ [17]. However, the results given in Figs. 1 and 2 indicate that there is no such enhancement of $\Delta$ in the ZF-$\mu$SR spectra below $T_c$ in Na$_{0.35}$CoO$_2$1.3H$_2$O, which demonstrates the absence of an additional spontaneous magnetic field above 0.1 Oe in the superconducting phase. This result strongly disfavors a pairing symmetry, like $d_{x^2-y^2} + id_{xy}$ in Na$_{0.35}$CoO$_2$1.3H$_2$O.

Prior to the muon Knight shift measurement, we performed weak transverse field $\mu$SR measurements to evaluate the effect of the flux line lattice (FLL) in the mixed state. At 374 Oe, the dumping rate of the spin precession signal slightly increases with decreasing temperature below $T_c$, which reflects the formation of FLL, as follows. In the mixed state of a type-II superconductor, an applied magnetic field ($H_{c1} < H < H_{c2}$, with $H_{c1}$ and $H_{c2}$ being the lower and upper critical field, respectively) induces FLL, where the internal magnetic field distribution is determined by the magnetic penetration depth ($\lambda$), the vortex core radius, and the lattice structure of FLL. When the system falls into the superconducting state with a typical length scale of $\lambda$ from $10^2$ to $10^3$ nm, it leads to additional dumping of the muon spin precession due to the inhomogeneity of the local field associated with the FLL state. Unfortunately, $\lambda$ in Na$_{0.35}$CoO$_2$1.3H$_2$O turned out to be too long to deduce detailed information about the structure of vortices, such as the core radius. In such a situation, one can represent the muon spin relaxation approximately by a simple Gaussian relaxation,
namely

\[ G_x(t) = A_s \left( f_s \exp \left( -\sigma_{FLL}^2 t^2 \right) + (1 - f_s) \right) \exp \left( -\sigma_s^2 t^2 \right) \cos(\omega_s t + \phi) \]

\[ + A_b \exp \left( -\Lambda_b t \right) \cos(\omega_b t + \phi), \tag{1} \]

where the first term corresponds to the signal from the specimen and the second term to that from the backing silver. The damping factor, \( \sigma_s = 0.21(1) \mu s^{-1} \) at 10 K, comes from the relaxation in the normal phase, which is determined by random nuclear dipolar fields, and is thus proportional to \( \Delta \), measured by ZF-\( \mu \)SR (i.e., \( \Delta = \sqrt{5} \sigma_s \)). \( f_s \) denotes the volume fraction of the superconducting part in the present specimen, which is estimated to be \( \sim 0.5 \) at 2.0 K from the fitting result. Note that the relaxation rate of backing silver (\( \Lambda_b \)) is negligibly small. The internal field distribution probed by muons is a convolution of the nuclear dipolar field distribution, and that due to FLL and \( \sigma_{FLL} \) indicate the effect of FLL.

Fig. 3 shows the temperature dependence of \( \sigma_{FLL} \) at 374 Oe, where \( \sigma_{FLL} \) increases with decreasing temperature below \( T_c \). In an isotropic superconductor with a hexagonal FLL, the second moment \( \langle \Delta B^2 \rangle \) is approximately given by [18]

\[ \langle \Delta B^2 \rangle = 2\sigma_{FLL}^2/\gamma \mu \approx 7.5 \times 10^{-4} (1 - h)^2 (1 + 3.9(1 - h)^2) \Phi_0^2 \lambda^{-4}, \tag{2} \]

where \( h = H/H_{c2} \) and \( \Phi_0 \) is the magnetic flux quantum. From these relations, the average penetration depth (\( \lambda \)) is estimated to be \( 7(1) \times 10^2 \) nm at 2 K under \( H = 374 \) Oe.

The presence of line nodes on the superconducting gap is suggested from recent Co-NQR measurements [6, 7]. Such a structure of the order parameter should be reflected on the temperature/field dependence of the penetration depth. Unfortunately, the observed \( \lambda \) in this compound is too long to obtain such information with reliable sensitivity.

The field inhomogeneity \( \langle \Delta B^2 \rangle \) decreases with increasing field due to the strong overlap of the flux lines and the increased contribution of vortex cores, leading to a diminishingly small spin relaxation (\( \sigma_{FLL} \sim 0 \)) at higher fields. This tendency is more enhanced when the superconducting order parameters has a nodal structure. In this situation, we can not distinguish the superconducting fraction from the normal fraction in the specimen, and thereby the spectra at 60 kOe can be analyzed by using the following simple relation:

\[ G_x(t) = A_s \exp(-\sigma_s^2 t^2) \cos(\omega_s t + \phi), \tag{3} \]

where we neglect the signal from the small amount of Apiezon-N grease, and omit the background term (\( A_b \)) because the measurements at 60 kOe are made without silver backing.
The relaxation rate ($\sigma_s$), where the obtained data are shown in Fig. 3 by open circles, is independent of the temperature, indicating that the effect of FLL is negligible. In this case, the frequency shift due to FLL is also estimated to be negligibly small (see below) and the muon Knight shift can be observed. Since $H_{c2}$ is reported to be 610 kOe with $T_c$ staying almost constant up to 40 kOe by a magnetization measurement[2], the system should be in the superconducting state at 60 kOe. In general, the muon Knight shift $K(T)$ is expressed as $K(T) = K_s(T) + K_{orb}$. Here, $K_s$ and $K_{orb}$ are the spin and orbital components of the Knight shift and only $K_s(T)$ is temperature dependent. Then, $K_s(T)$ is determined by the gradient of the muon Knight shift versus the magnetic susceptibility ($K-\chi$) plot, as shown in Fig. 4(a), irrespective of $K_{orb}$ (which was set to zero in this analysis). Fig. 4(b) shows the temperature dependence of $K_s(T)$ and the uniform susceptibility at 10 kOe in a randomly oriented sample of Na$_{0.35}$CoO$_2$1.3H$_2$O. The muon Knight shift decreases with decreasing temperature below 100 K, and levels off below 10K. Above 10 K, $K_s(T)$ is proportional to the uniform susceptibility, which clearly indicates that the upturn of the $\chi(T)$ below $\sim$ 100 K is not due to impurities, but due to some intrinsic origin. The spin part of the muon Knight shift is expressed as $K_s = A_{hf}\chi$, where $A_{hf}$ is the hyperfine coupling constant. From the above relation, $A_{hf}$ is estimated to be $\sim -134$ Oe/$\mu_B$. It should be noted that the anisotropic term of the Knight shift, or the so-called powder pattern, is not seen in the spectra. This implies that the anisotropy of the Knight shift is too small for the present resolution. In the case of s-wave pairing superconductivity, $K_s$ decreases to zero with decreasing temperature following the Yosida function[19]. However, as shown in the inset of Fig. 4, the muon Knight shift does not show any appreciable reduction below $T_c$. Indeed, the average of $K_s$ for 4.7-10 K ($> T_c$) is $-14.4(5)$ ppm which is in good agreement with $-15.1(5)$ ppm for 2.0-4.4 K ($< T_c$). This result shows that the spin susceptibility is unchanged in the superconducting state.

Since the observed muon Knight shift is negative, there remains a possibility that the reduction of $K_s$ below $T_c$ may be cancelled by the diamagnetic shift upon the formation of FLL. We estimated the magnitude of such a diamagnetic shift by taking account of the effects of a dense overlap of vortices and the Doppler shift; the latter is present when the superconducting gap has nodes, leading to a further enhancement of $\lambda[20]$. This is reasonable considering the recent NQR measurements[6, 7], suggesting line nodes in this compound. Our simulation yielded that $\lambda \approx 12$ $\mu$m, where the associated diamagnetic shift by the FLL
formation is less than 2.8 ppm at 60 kOe, which is too small to cancel out the predicted effect due to spin singlet superconductivity. Thus, we conclude that the result given in Fig. 4 is entirely attributed to $K_s$.

Here, we discuss the symmetry of the Cooper pair. We observed no significant reduction of the spin part of the muon Knight shift within the error bar below 10 K. If we assume that the residual density of state is 35%, as estimated from one of the reported NMR measurements, the reduction in the Knight shift is too small for the spin singlet superconductivity. This suggests that the paring of the Cooper pair is a spin triplet state, which is in line with the result by Waki et al., who observed no reduction of the $^{59}$Co Knight shift below $T_c$. Quite recently, a nearly ferromagnetic spin fluctuation was proposed by Ishida et al. These observations seem to be promising for spin triplet superconductivity from the analogy of the superfluidity of $^3$He. Our result is inconsistent with the Knight-shift results in Ref [4], which was measured in 15 kOe. The inconsistency might be related to the difference of the applied field.

Theoretically, $p + ip$ or $f$ wave superconductivity is suggested for the spin triplet superconductivity. Since our result of ZF-$\mu$SR excludes the possibility of time-reversal symmetry breaking superconductivity, the chiral $p$-wave superconductivity is strongly disfavored. When the spin triplet $d$-vector is pinned to some direction, it is expected that $1/3(d//z$-axis) or $2/3 (d \perp z)$ of the muon Knight shift would decrease in a polycrystalline specimen. The absence of such a reduction in the Knight shift suggests that the effective spin-orbit coupling is much weaker than 60 kOe, leading to an alignment of the $d$ vector against the external field.

In summary, we have demonstrated by ZF-$\mu$SR that no static magnetism appears in Na$_{0.35}$CoO$_2$1.3H$_2$O down to 2K. This leads us to conclude that the time-reversal symmetry is preserved in the superconducting order parameter. The muon Knight shift at 60 kOe exhibits no obvious reduction below $T_c$ down to 2 K, suggesting that the spin part of the Cooper pair is a spin triplet state.

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FIG. 1: ZF-µSR time spectra in Na$_{0.35}$CoO$_2$1.3H$_2$O, above and below $T_c$. A spectrum observed at 10 K in a deuterated specimen is also shown for a comparison.

FIG. 2: Temperature dependence of the nuclear dipolar width ($\Delta$) for two specimens from different batches. Inset: temperature dependence of magnetic susceptibility with field cooling (FC) and zero field cooling (ZFC) conditions for the sample #2.

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FIG. 3: Temperature dependence of $\sigma_{FLL}$ at 374 Oe and $\sigma_s$ at 60 kOe in Na$_{0.35}$CoO$_2$1.3H$_2$O. Solid lines are guide for eyes.
FIG. 4: (a) Muon Knight shift versus susceptibility plot. (b) Temperature dependence of the spin part of the muon Knight shift $K_s$ (filled dot) and susceptibility (solid line). The susceptibility was measured at 10 kOe.

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Muon Spin Polarization

Time (μs)

ZF-μSR

\[ \text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O} \quad 10K \]

\[ \text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O} \quad 2K \]

\[ \text{Na}_{0.35}\text{CoO}_2 \cdot 1.4\text{D}_2\text{O} \quad 10K \]

Fig. 1
Fig. 2

Sample 1
Sample 2

\( \text{Na}_x \text{CoO}_2y\text{H}_2\text{O} \)

Dipolar Width (MHz)

Temperature (K)

\(\chi\) (emu/mol)

Temperature (K)

Sample 2
15 Oe

FC
ZFC
Fig. 4(a)
Fig. 4(b)

muon Knight Shift $K_s$ (ppm)

Temperature (K)

Susceptibility (emu/mol)