Magnetic and superconducting nature of $\text{Na}_{0.35}\text{CoO}_2 \cdot y\text{H}_2\text{O}$ and $\text{Na}_{0.35}\text{CoO}_2 \cdot y\text{D}_2\text{O}$ investigated by muon-spin spectroscopy

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In order to clarify the carrier density dependence of the microscopic magnetic nature in $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$, we have performed a positive muon-spin rotation/relaxation ($\mu^+\text{SR}$) study of H_2O and D_2O intercalated samples. Based on the zero-field (ZF) $\mu^+\text{SR}$ measurements, there was no clear difference between the two superconducting phases (SCI and SCII). This is also likely to exclude the exotic scenario for the superconductivity of the SCII phase, in which the superconducting state breaks the time-reversal symmetry of the Cooper pairs, resulting in the appearance of a weak internal magnetic field below T_c . Furthermore, the ZF spectrum for the H_2O intercalated sample exhibits a clear oscillation in the whole T range measured (1.4–100 K), suggesting the formation of “[H_3O] $^+$ -like” $\text{H}_2\mu^+\text{O}$ ions in the sample. The absence of the oscillation in the D_2O -intercalated sample also evidences the presence of the $\text{H}_2\mu^+\text{O}$ complex. Considering the fraction of the $\text{H}_2\mu^+\text{O}$ signal, we have demonstrated the coexistence of [H_3O] $^+$ ions and H_2O in this compound.

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I. INTRODUCTION

The discovery of superconductivity (SC) in water-intercalated sodium cobalt dioxides, $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$,¹ leads to the question on the role of H_2O in generating the SC state and on its nature, i.e., conventional or exotic.^{2–4} Shortly after the discovery, the presence of oxonium ions ($[\text{H}_3\text{O}]^+$) in $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ was proposed from chemical titration analyses.⁵ That is, the Co valence (V_{Co}) was estimated as ~ 3.46 for the $x=0.36$, $y=1.3$ sample, while it was expected that $V_{\text{Co}} \sim 3.64$ based on the compositional analysis. This proposal is consistent with the Curie-Weiss behavior at high T , because a Pauli-paramagnetic behavior is expected for $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ with $V_{\text{Co}} \geq 3.5$.^{6,7} Since then, the accurate formula of water-intercalated Na_xCoO_2 is represented as $\text{Na}_x(\text{H}_3\text{O})_z\text{CoO}_2 \cdot y\text{H}_2\text{O}$. This means that there are at least two predominant parameters that govern the carrier concentration of $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$, namely, the Na content x and the $[\text{H}_3\text{O}]^+$ content z , resulting in difficulty to adjust V_{Co} . Furthermore, there is no direct experimental evidence for the coexistence of $[\text{H}_3\text{O}]^+$ and H_2O since it is difficult to distinguish them in transition metal oxides.

Recently, Ohta *et al.*⁸ found a route to control the carrier density of the CoO_2 plane by keeping the $\text{Na}_x(\text{H}_3\text{O})_z\text{CoO}_2 \cdot y\text{H}_2\text{O}$ sample in a humid atmosphere for different amount of time. The electronic and magnetic phase diagram of $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ ($x \sim 0.35$, $y \sim 1.3$) was subsequently clarified by both nuclear quadrupole resonance (NQR) and magnetic susceptibility (χ) measurements (see Fig. 1).^{9–13} That is, as the ^{59}Co -NQR frequency (ν_{Q3}) increases from 12.0 to 12.4 MHz, a superconducting (SCI) phase with $T_c \leq 4.7$ K appears, and then, a magnetic (M)

phase with $T_m \leq 6$ K exists in the ν_{Q3} range between 12.42 and 12.55 MHz, and finally, a second superconducting (SCII) phase with $T_c \leq 4.5$ K appears again until $\nu_{\text{Q3}} = 12.74$ MHz (see Fig. 1). Here, ν_{Q3} is proportional to the distortion of the CoO_6 octahedron, and as a result, ν_{Q3} is thought to be a good indicator for the carrier density in the CoO_2 plane. The origin of SCI and SCII phases and the difference between them are, however, not fully understood, in spite of recent NMR work^{14,15} and a theoretical treatment.^{16–21}

In contrast to NMR, positive muon-spin rotation and relaxation ($\mu^+\text{SR}$) provides information on microscopic magnetic environment for a sample in the vicinity of the implanted muons in the wide field range from a few oersted (originating from nuclear magnetic moments) up to several

FIG. 1. (Color online) The magnetic phase diagram of hexagonal $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ determined by ^{59}Co NQR and susceptibility measurements (Ref. 9). Open circles represent the H_2O -intercalated samples used for the present $\mu^+\text{SR}$ study and open triangles the D_2O intercalated samples. The present M samples did not exhibit a superconducting transition down to the lowest T measured (1.8 K).

tesla (from electron spins). Moreover, although μ^+ SR measurements were performed for the SC samples,^{22–24} it is difficult to know whether they are the SCI or SCII phase without their ν_{Q3} . As a result, there are no studies covering the complete phase diagram of $\text{Na}_x(\text{H}_3\text{O})_z\text{CoO}_2 \cdot y\text{H}_2\text{O}$. We have, therefore, carried out a systematic μ^+ SR study for the three phases using both H_2O and D_2O intercalated samples. Here, we demonstrate the direct evidence for the coexistence of $[\text{H}_3\text{O}]^+$ and H_2O and the absence of any crucial difference in the microscopic magnetic nature between the SCI and SCII phase.

II. EXPERIMENT

The $\text{Na}_x(\text{H}_3\text{O})_z\text{CoO}_2 \cdot y\text{H}_2\text{O}$ and $\text{Na}_x(\text{D}_3\text{O})_z\text{CoO}_2 \cdot y\text{D}_2\text{O}$ samples were prepared by soft chemical methods and the details are reported in Ref. 8. The obtained samples were confirmed to be in a single phase of $\text{Na}_x(\text{H}_3\text{O})_z\text{CoO}_2 \cdot y\text{H}_2\text{O}$ or $\text{Na}_x(\text{D}_3\text{O})_z\text{CoO}_2 \cdot y\text{D}_2\text{O}$ by powder x-ray diffraction. Prior to μ^+ SR measurements, their magnetization was measured by a superconducting quantum interference device magnetometer with magnetic field $H=20$ Oe. Their ^{59}Co -NQR spectrum was also measured to estimate T_c and the NQR frequency ν_{Q3} . Typical results are shown in Fig. 1. All the samples used for the μ^+ SR measurements were confirmed to obey the phase diagram; that is, open circles for the H_2O intercalated samples and open triangles for the D_2O intercalated samples. All six samples were kept inside a refrigerator and consequently packed into a gold O-ring sealed powder cell, and then, transferred to the μ^+ SR facility in a cool box. The μ^+ SR spectra were measured at the surface muon beam lines using the MuSR spectrometer of ISIS in U.K. and at the LAMPF spectrometer of TRIUMF in Canada, using He flow-type cryostats in the T range between 1.4 and 100 K. The experimental techniques were described elsewhere.²⁵

III. RESULTS

Figure 2 shows the zero field (ZF)- μ^+ SR time spectra for the six water-intercalated samples, i.e., the H_2O intercalated SCI, M, and SCII samples and D_2O intercalated SCI, M, and SCII samples. All the spectra show mainly a Kubo-Toyabe (KT) behavior due to an internal magnetic field caused by the nuclear magnetic moments of ^{23}Na , ^{59}Co , ^1H , and ^2H ($=\text{D}$). In addition, the zero-field (ZF) spectra for the H_2O intercalated samples exhibit a clear oscillation with a small amplitude (~ 0.02); that is, for the H_2O intercalated SCI sample, the ZF spectrum (the bottom one) has a first minimum around 4 μs and a second minimum around 9 μs . Since the initial asymmetry (A_0) is the maximum value for the present setup (~ 0.28) for all the ZF spectra and the overall relaxation is described well by a KT behavior, there is no magnetic order for the water-intercalated samples even at 1.4 K, as already reported. The oscillation should, therefore, be due to the nuclear magnetism. Furthermore, the absence of the oscillation in the spectra for the D_2O intercalated samples suggests the formation of a three spin-one-half ($S=1/2$) system between H and μ^+ .

FIG. 2. (Color online) The ZF- μ^+ SR time spectra at the lowest T measured for the three H_2O intercalated samples (SCI, M, and SCII from bottom) and three D_2O intercalated samples (SCI, M, and SCII from bottom). Solid lines for the H_2O intercalated samples represent the fitting result using Eq. (1) while that for the D_2O intercalated samples using Eq. (3). Each spectrum is offset by 0.05 for clarity of display. These spectra were obtained in ISIS.

A. H_2O -intercalated samples

The correct formula, $\text{Na}_x(\text{H}_3\text{O})_z\text{CoO}_2 \cdot y\text{H}_2\text{O}$ and/or $\text{Na}_x(\text{D}_3\text{O})_z\text{CoO}_2 \cdot y\text{D}_2\text{O}$, naturally indicate that the implanted μ^+ exists in the vicinity of the H_2O (D_2O) molecule to make stable oxoniumlike $[\text{H}_2\mu\text{O}]^+([\text{D}_2\mu\text{O}]^+)$ ions. Indeed, past dipole field calculations suggested that μ^+ locates between the CoO_2 plane and the H_2O layer.²² In fact, the ZF spectrum for the H_2O intercalated samples were well fitted by a combination of three signals; namely, a dynamic KT function $[G^{\text{DGKT}}(t)]$, a signal for three spin-a-half system with a regular triangular configuration $[G^{\text{tri}}(t)]$, and an offset signal from the fraction of muons stopped mainly in the sample holder, which is made of high-purity aluminum

$$A_0 P_{\text{ZF}}(t) = A_{\text{KT}} G^{\text{DGKT}}(\Delta, \nu, t) + A_{\text{H}_2\mu\text{O}} G^{\text{tri}}(t) \exp\left(-\frac{\sigma_{\text{H}_2\mu\text{O}}^2 t^2}{2}\right) + A_{\text{BG}}, \quad (1)$$

where A_0 is the initial asymmetry, A_{KT} , $A_{\text{H}_2\mu\text{O}}$, and A_{BG} are the asymmetries associated with the three signals. Δ is the static width of the local field distribution at the disordered sites, and ν is the field fluctuation rate. When $\nu=0$, $G^{\text{DGKT}}(t, \Delta, \nu)$ is the static Gaussian KT function $G_{\text{zz}}^{\text{KT}}(t, \Delta)$. $\sigma_{\text{H}_2\mu\text{O}}$ is the Gaussian relaxation rate for the $A_{\text{H}_2\mu\text{O}}$ signal.

The analytical form for the collinear three spin-one-half system was proposed originally for the F- μ -F system in alkali fluorides.²⁶ Similar systems with other anions e.g., “ $\text{H}\mu^+\text{H}$ ” and/or “ $\text{H}\mu^+$ ” have been reported in a Kagomé compound $\text{ZnCu}_3(\text{OH})_6\text{Cl}_3$,²⁷ in a layered cobalt dioxide $[\text{Ca}_{0.85}\text{OH}]_{1.16}[\text{CoO}_2]$,²⁸ in NaAlH_4 ,²⁹ and in metal borohydrides $M(\text{BH}_4)_2$.³⁰ However, for a triangular three spin-one-

FIG. 3. (Color online) Variation in the ZF- μ^+ SR spectrum with T for the H_2O intercalated SCII sample. Solid lines represent the fitting result using Eq. (1). Each spectrum is offset by 0.05 for clarity of display. The spectrum obtained below T_c (~ 4.5 K) is essentially the same to those obtained above T_c .

half system, $G^{\text{tri}}(t)$ was, to our knowledge, not analytically derived so far. Based on a numerical simulation, $G^{\text{tri}}(t)$ is represented by³¹

$$G^{\text{tri}}(t) = 0.28570 + 0.23429 \cos(1.92058kt) \\ + 0.13719 \cos(1.75341kt) + 0.05169 \cos(1.15184kt) \\ + 0.02750 \cos(0.76874kt) + 0.18697 \cos(0.60156kt) \\ + 0.07655 \cos(0.16718kt). \quad (2)$$

Here $k = (\sqrt{2}/d_{\text{H-}\mu})^3$, in which $d_{\text{H-}\mu}$ is the distance between H and μ , i.e., the edge length of the regular triangle formed by two H and one μ . Note that, since the gyromagnetic ratio of μ^+ (γ_μ) and proton (γ_{H}) and the permeability of vacuum (μ_0) are included in the numerical constants, $d_{\text{H-}\mu}$ is in Angströms and t in microseconds in Eq. (2).

Interestingly, the oscillatory signal in the ZF spectrum does not change with T , as seen in Fig. 3 for the H_2O intercalated SCII sample. Indeed, the fit using Eq. (1) demonstrates that all the μ^+ SR parameters of the $A_{\text{H}_2\mu\text{O}}$ signal—i.e., $A_{\text{H}_2\mu\text{O}}$, k , and $\sigma_{\text{H}_2\mu\text{O}}$ are roughly T independent for the whole T range measured (see Fig. 4). We, therefore, attempted to fit all the ZF spectra using common A_{KT} , $A_{\text{H}_2\mu\text{O}}$, A_{BG} , k , and $\sigma_{\text{H}_2\mu\text{O}}$ in Eq. (1). Such a “simultaneous fit” yielded $A_{\text{KT}} = 0.1695 \pm 0.0008$, $A_{\text{H}_2\mu\text{O}} = 0.0474 \pm 0.0007$, $A_{\text{BG}} = 0.0653 \pm 0.0002$, $k/2\pi = (0.0872 \pm 0.0003)$ MHz, and $\sigma_{\text{H}_2\mu\text{O}} = (0.110 \pm 0.002) \times 10^6 \text{ s}^{-1}$, respectively. Then, d is estimated as $1.731 \pm 0.002 \text{ \AA}$, which is consistent with the edge length of the regular triangle of the H ions in the oxonium ion ($1.6296 \text{ \AA}$). Note that, considering the crystal structure of the water-doped $\text{Na}_{0.35}\text{CoO}_2$, there are no stable muon sites to form a linear H- μ -H bond between the neighboring water molecules (see Appendix).

FIG. 4. (Color online) T dependencies of μ^+ SR parameters for the H_2O intercalated SCII sample; (a) three asymmetries, A_{KT} , A_{BG} , and $A_{\text{H}_2\mu\text{O}}$, (b) the field distribution width (Δ), field fluctuation rate (ν), and Gaussian relaxation rate of the $\text{H}_2\mu\text{O}$ signal ($\sigma_{\text{H}_2\mu\text{O}}$), and (c) the oscillation frequency [$k/(2\pi)$] of the $\text{H}_2\mu\text{O}$ signal. The data were obtained by fitting the ZF spectra using Eq. (1).

Figure 5 shows the T dependencies of Δ and ν for the H_2O intercalated SCII sample obtained by such a simultaneous fit. Both Δ and ν are found to be T independent below 15 K, despite the fact that $T_c = 5$ K. This means that the SCII phase is, in principle, nonmagnetic, as in the case for SCI. However, as T increases from 15 K, Δ and ν decrease

FIG. 5. (Color online) T dependencies of Δ and ν for the H_2O intercalated SCII sample. The data were obtained by simultaneous fitting of the ZF spectra using Eq. (1). The common parameters, A_{KT} , $A_{\text{H}_2\mu\text{O}}$, A_{BG} , $k/(2\pi)$, and $\sigma_{\text{H}_2\mu\text{O}}$, are listed in Table I. Also, Δ and ν for $\text{Na}_{0.4}\text{CoO}_2$ are plotted as large diamonds, for comparison.

FIG. 6. (Color online) T dependencies of (a) and (c) Δ , and (b) and (d) ν for the water-intercalated $\text{Na}_{0.35}\text{CoO}_2$ samples. The data in (a) and (b) were obtained by simultaneous fitting the ZF spectra using Eq. (1). The common parameters are listed in Table I.

slightly, probably due to a thermally activated motion/vibration of the lattice and/or thermal expansion. Indeed, the decrease in Δ with T is also observed for the related compound, Li_xCoO_2 with $x \leq 1$.³² It should be noted that, since $\nu \sim 0.23 \times 10^6 \text{ s}^{-1} \sim 0.53 \times \Delta$ even at the lowest T measured, the nuclear magnetic field is still fluctuating.

In order to know the effect of the intercalated water on Δ and ν , the data for $\text{Na}_{0.4}\text{CoO}_2$, from which the present water-intercalated samples were prepared, are also shown in Fig. 5. Due to the large nuclear magnetic moment of H, Δ increases by $\sim 0.2 \times 10^{-6} \text{ s}^{-1}$ ($= 2.4 \text{ Oe}$) in the whole T range measured, while ν increases only by $\sim 0.04 \times 10^{-6} \text{ s}^{-1}$ ($= 6.4 \text{ kHz}$). This means that ν for the H_2O intercalated SCII sample is mainly determined by the fluctuation of Co nuclear moments plus an additional minor contribution from the water, probably due to a dynamic motion of the H_2O molecule.³³ Considering the fact that $\nu \sim 0.1 \times 10^6 \text{ s}^{-1}$ for $\text{Li}_{1/3}\text{CoO}_2$ (Ref. 34) and $\nu \sim 0$ for $\text{K}_{4/7}\text{CoO}_2$ (Ref. 35) at 1.8 K, such fluctuation could play a significant role for the appearance of superconductivity in water-intercalated Na_xCoO_2 .

The ZF spectra for the other two H_2O intercalated samples, namely, the SCI and M phase, were also simulta-

neously fitted using Eq. (1). Figures 6(a) and 6(b) show the T dependencies of Δ and ν for the three samples, and Table I summarizes their common parameters. Since both $\Delta(T)$ and $\nu(T)$ curves for the SCI sample are essentially the same to those for the SCII sample, there are no clear differences in the microscopic magnetic environment at the muon sites between the SCI and SCII sample. This is also likely to exclude the exotic scenario for the superconductivity of the SCII phase, in which the superconducting state breaks time-reversal symmetry of the Cooper pairs, resulting in the appearance of a weak internal magnetic field below T_c . In contrast to the SC samples, as T decreases from 50 K, Δ for the H_2O intercalated M samples remains at the same value as the SC samples down to 6 K, and then, Δ increases with decreasing its slope ($d\Delta/dT$) with further lowering T . This clearly demonstrates the appearance of an internal magnetic field (H_{int}) below T_m , although the magnitude of H_{int} is found to be comparable to that of the nuclear magnetic field. It should be noted that ν is T independent regardless of T_m .

B. D_2O -intercalated samples

Since the spin angular momentum of D is unity, the $\text{D}_2\mu\text{O}$ molecule no longer induces a clear oscillation in the ZF

TABLE I. $\mu^+\text{SR}$ parameters for the three H_2O intercalated samples estimated from the simultaneous fit using Eq. (1). The ^{59}Co -NQR frequency (ν_{Q3}) for all three samples is also shown for reference.

Phase	ν_{Q3} (MHz)	A_{KT}	$A_{\text{H2}\mu\text{O}}$	A_{BG}	$k/2\pi$ (MHz)	$d_{\text{H}-\mu}$ (Å)	$\sigma_{\text{H2}\mu\text{O}}$ (10^6 s^{-1})
SCI	12.3	0.1548 ± 0.0012	0.0578 ± 0.0011	0.0790 ± 0.0003	0.0870 ± 0.0004	1.727 ± 0.003	0.127 ± 0.002
M	12.525	0.163 ± 0.006	0.0507 ± 0.0005	0.0828 ± 0.006	0.0865 ± 0.0012	1.816 ± 0.002	0.201 ± 0.002
SCII	12.575	0.1692 ± 0.0012	0.0477 ± 0.0011	0.0654 ± 0.0002	0.0868 ± 0.0003	1.731 ± 0.002	0.110 ± 0.002

FIG. 7. (Color online) ZF- and two LF- μ^+ SR spectra for the D₂O-intercalated SCII sample measured at 10 K. The magnitude of LF was 5 and 10 Oe. Solid lines represent the simultaneous-fit result by Eq. (3).

μ^+ SR time spectrum but would provide a relaxation.³⁶ Furthermore, although the muons are most likely to locate near D₂O as in the case for the H₂O intercalated sample, the nuclear magnetic moments of the next-nearest Na and/or Co are expected to play a significant role for the muon-spin depolarization. This is because the nuclear magnetic moment of D is much smaller than that of H. As a result, the ZF spectrum could be explained by a combination of two KT signals. However, as seen in Fig. 2, the ZF spectra for the three D₂O intercalated samples exhibit one broad minimum around 10 μ s for the SCI and SCII phase and 5 μ s for the M phase. This makes the analysis very difficult, particularly for separating the two KT signals. Therefore, the ZF spectra were fitted by a combination of a KT signal, a Gaussian damped cosine oscillation and an offset signal, instead

$$A_0 P_{ZF}(t) = A_{KT} G^{DGKT}(\Delta, \nu, t) + A_m \cos(\omega_m t + \phi_m) \exp\left(-\frac{\sigma_m^2 t^2}{2}\right) + A_{BG}. \quad (3)$$

Here, we assume that a Gaussian relaxing cosine oscillation is a reasonable approximation for a Gaussian KT signal, particularly for the signal with a small amplitude. Considering the situation of the H₂O intercalated sample, we simultaneously fitted the ZF and two longitudinal field (LF) μ^+ SR spectra for the D₂O intercalated samples at 10 K, which roughly corresponds to $2 \times T_c$ (or $2 \times T_m$), to determine A_{BG} , at first (see Fig. 7 and Table II). For the simultaneous fit, we

also assumed that only ω_m changes with LF but other parameters are common regardless of LF. Then, using the obtained A_{BG} , the ZF spectra were fitted by Eq. (3).

Figures 6(c) and 6(d) show the T dependencies of Δ and ν for the three D₂O intercalated samples. Δ for the three SC samples and ν for the three samples are roughly T independent in the whole T range measured. However, only the $\Delta(T)$ curve for the M sample shows a order-parameterlike T dependence below T_m , as in the case of the H₂O intercalated M sample. The overall behavior of the D₂O intercalated samples is, thus, found to be the same to that of the H₂O intercalated samples. Note that the magnitude of Δ and ν for the D₂O intercalated samples above T_c/T_m are comparable to those for Na_{0.4}CoO₂ (see Fig. 5). This means that the effect of the nuclear magnetic moment of D on μ^+ SR parameters is negligibly small, as expected.

IV. DISCUSSION

A. Three phases

For both the H₂O and D₂O intercalated samples, the $\Delta(T)$ and $\nu(T)$ curves for the SCI phase are roughly the same to those for the SCII phase. This indicates that the SCI phase is very similar to the SCII phase, particularly under ZF and low magnetic field below 10 Oe. This means the absence of a spontaneous internal magnetic field in the SCII phase, as well as in the SCI phase. Electronic-structure calculations proposed singlet s -wave superconductivity for SCI but triplet p - or f -wave superconductivity for SCII.²¹ Note that the spin-triplet superconductivity is sometimes accompanied by the breaking of time-reversal symmetry,³⁷ resulting in the appearance of an internal magnetic field below T_c . However, based on the present μ^+ SR results, such a spin-triplet superconductivity is most unlikely for the SCII phase, as already mentioned above.

In order to further establish the Cooper pair symmetry for the SCII phase, muonic Knight shift measurements at low T (Refs. 22, 38, and 39) are necessary to determine whether the singlet s -wave superconductivity or the triplet p - or f -wave superconductivity is reasonable for SCII. Unfortunately, such an experiment is currently not feasible because of challenges involved in mounting an unstable, appropriate sized, sample into the tight geometry of a spectrometer required for high transverse field measurements. Recent Co-NMR measurements, however, proposed that the nature of the SCII phase is very similar to that of the SCI phase.^{9,15} This is consistent with the present μ^+ SR result under low magnetic fields.

TABLE II. asymmetries for the three D₂O intercalated samples estimated from the simultaneous fit at 10 K for one ZF and two LF spectra using Eq. (3). The ⁵⁹Co-NQR frequency (ν_{Q3}) for all three samples is also shown for reference.

Phase	ν_{Q3} (MHz)	A_{KT}	A_m	A_{BG}
SCI	12.35	0.18186 ± 0.0001	0.0319 ± 0.0001	0.0662 ± 0.0001
M	12.475	0.1855 ± 0.0009	0.0307 ± 0.0008	0.0761 ± 0.0007
SCII	12.7	0.1828 ± 0.001	0.0359 ± 0.0010	0.0796 ± 0.0007

Now, we discuss the *so-called* “M” phase. It should be noted that the A_{KT} does not change at T_m [see Fig. 4(a)], confirming the absence of any kind of magnetic order observable by μ^+ SR below T_m . Furthermore, since the ZF spectrum can be fitted by one KT signal and two small T -independent signals both above and below T_m , the whole volume of the sample is found to undergo the transition from a high- T paramagnetic phase to the M phase at T_m . This clearly excludes the possibility that small and *inhomogeneous* magnetic moments, which could be induced by charge-density-wave order or charge disproportionation, are frozen below T_m .^{15,40} But, it is demonstrated that small magnetic moments suddenly appear in the whole sample *homogeneously* in a static fashion because the field fluctuation rate (ν) is found to be T -independent across T_m . As seen in Figs. 5 and 6, since ν for the H_2O intercalated M sample is comparable to ν for $Na_{0.4}CoO_2$, the origin ν is most likely the fluctuation of the Co nuclear moments. Therefore, the magnetic moments appearing below T_m should be static.

Although the origin of the appearance of the magnetic moments is still not clarified, we here wish to speculate about it. For the D_2O intercalated SCI phase, neutron and electron diffraction measurements found a superlattice reflection,⁴¹ which was explained by a commensurate (C) modulation of the guest layer, $Na_{0.35}1.3D_2O$, against the CoO_2 plane.⁴² Here, the increase in ν_{Q3} (see Fig. 1) is induced by the distortion of the CoO_6 octahedra due to the change in carrier density. The change in ν_{Q3} , thus, would imply a mismatch between the guest layer and the CoO_2 plane. Considering the stability of the C structure, as ν_{Q3} increases, a C phase is expected to change into another C phase via an IC phase in a narrow ν_{Q3} range, as in the case for discommensuration.⁴³ Only for the IC phase, which is assumed to correspond to the M phase, the charge distribution of the CoO_2 plane is likely to be perturbed by the IC modulation, resulting in the appearance of small magnetic moments in the whole compound and the annihilation of superconductivity. In order to confirm this hypothesis, it would be necessary to perform neutron diffraction measurements on the M sample at low T .

B. Formation of $H_2\mu O$

Positive muons naturally do not locate near $[H_3O]^+$ ions but near H_2O so as to make $H_2\mu^+O$ ions. Hence, the ratio $[A_{H_2\mu O}/(A_{KT}+A_{H_2\mu O})]$, which ranges between 0.22 and 0.27, would correspond to the ratio, $H_2O/(H_2O+[H_3O]^+)$. However, since the majority of the implanted muons feel the random nuclear magnetic field—i.e., the KT field distribution, such ratio should be less than $H_2O/(H_2O+[H_3O]^+)$. In fact, based on composition and oxidation state analysis, $H_2O/(H_2O+[H_3O]^+)$ for the SCI phase is estimated as 0.55–0.8 [or $H_3O/(H_2O+[H_3O]^+)=0.45–0.2$].^{5,44} In other words, although μ^+ forms a unique oxoniumlike $[H_2\mu O]^+$ three spin-one-half system, it is difficult to determine the H_2O content in the sample by μ^+ SR.

Nevertheless, we wish to emphasize that the presence of an $H_2\mu O$ oscillation directly evidences the existence of $[H_3O]^+$ ions in water-intercalated Na_xCoO_2 because μ^+ is a

light isotope of H^+ . More correctly, since $m_H \sim 9 \times m_\mu$, where m_H is the mass of H^+ and m_μ is the mass of μ^+ , the thermal vibration of μ^+ in $[H_2\mu O]^+$ is three times larger than that of H^+ in $[H_3O]^+$. This means that $[H_2\mu O]^+$ is probably more unstable than $[H_3O]^+$. Therefore, the presence of $[H_2\mu O]^+$ indicates that $[H_3O]^+$ is even more likely stable in water-intercalated Na_xCoO_2 . Furthermore, assuming that the $[H_3O]^+$ ion hinders the formation of $H_2\mu O$ at the nearest-neighbor H_2O molecules due to its positive charge, the obtained $A_{H_2\mu O}/(A_{KT}+A_{H_2\mu O})$ would be more acceptable. This is because the NaO_6 prism is formed in the $Na_{0.35}1.3H_2O$ layer.^{41,44} As a result, for a certain H_2O , the number of the nearest-neighbor H_2O molecules is estimated as two or four, which depends on the Na content.⁴¹ In summary, we have clarified the coexistence of H_2O and $[H_3O]^+$ in the water-intercalated Na_xCoO_2 through the formation of $H_2\mu O$ by means of μ^+ SR.

V. CONCLUSIONS

In order to investigate the difference between two superconducting phases (SCI and SCII) of water-intercalated Na_xCoO_2 , we have measured ZF μ^+ SR spectra both for the $Na_xCoO_2 \cdot yH_2O$ and $Na_xCoO_2 \cdot yD_2O$ with $x \sim 0.35$ and $y \sim 1.3$ powder samples. The microscopic magnetism of the SCII phase was found to be very similar to that of the SCI phase, indicating an absence of time-reversal symmetry breaking for the Cooper pairs in the SCII phase. On the other hand, for the M phase, which ranges between the SCI and SCII phase below about 6 K ($=T_m$) in the T vs carrier density phase diagram, a random and small magnetic field was detected below T_m both for the H_2O and D_2O intercalated samples. The appearance of the M phase could be explained by the concept, “discommensuration,” due to the mismatch between the $Na_{0.35}(H_2O)_{1.3}/Na_{0.35}(H_2O)_{1.3}$ layer and the CoO_2 plane.

Furthermore, we found a clear oscillation in the ZF spectra only for the H_2O intercalated samples, but no oscillations for the D_2O intercalated samples. The volume fraction of the oscillatory signal was estimated as 22–27 % and the rest of muons were found to “see” a small and random nuclear magnetic field. According to numerical analyses of the ZF spectra, the origin of the oscillation was clarified as the formation of “[H_3O]⁺-like” $H_2\mu^+O$ ions. The fact that only the 22–27 % muons form the $H_2\mu^+O$ ions indicated the coexistence of H_2O and $[H_3O]^+$ in these compounds.

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FIG. 8. (Color online) Fit results of the ZF- μ^+ SR spectrum for the H_2O -intercalated SCII sample at 1.4 K. The fit using a $\text{H}_2\mu\text{O}$ signal provides a reasonable result while the fit using a $\text{H}-\mu$ signal does not reproduce the second maximum around 11 μs . Since the fit was performed to minimize χ^2 , reduced $\chi^2(=\chi^2/N)$ is shown for comparison, where N is degree of freedom.

APPENDIX: FIT OF THE ZF SPECTRUM

In order to explain the origin of the oscillatory signal in the ZF- μ^+ SR spectra for the H_2O intercalated samples, we also attempted to fit the spectra using the following two signals; namely, one is the signal for the collinear three spin-one-half system ($P_{\text{H}\mu\text{H}}$), and the other is the two spin-one-half system ($P_{\text{H}\mu}$). The former corresponds to the signal from the muons locating at the middle of two H_2O molecules while the latter corresponds to the signal from the muons forming a H_2O -like $\text{H}\mu\text{O}$ molecule. The two signals are represented by²⁶

$$P_{\text{H}\mu\text{H}}(t) = \frac{1}{2} + \frac{1}{6}\cos(\sqrt{3}\omega_d t) + \frac{1+1/\sqrt{3}}{6}\cos\left(\frac{3+\sqrt{3}}{2}\omega_d t\right) + \frac{1-1/\sqrt{3}}{6}\cos\left(\frac{3-\sqrt{3}}{2}\omega_d t\right) \quad (\text{A1})$$

and

$$P_{\text{H}\mu}(t) = \frac{1}{6} + \frac{1}{6}\cos(\omega_d t) + \frac{1}{3}\cos\left(\frac{1}{2}\omega_d t\right) + \frac{1}{3}\cos\left(\frac{3}{2}\omega_d t\right), \quad (\text{A2})$$

where ω_d is the muon precession frequency due to the nuclear dipole field of the proton in the $\text{H}-\mu^+$ bond. From ω_d , it is possible to calculate the distance d between the μ^+ and the nucleus according to²⁶

$$\omega_d \equiv 2\pi \cdot f_d = \mu_0 \hbar \frac{\gamma_\mu \gamma_N}{4\pi d^3}. \quad (\text{A3})$$

Here γ_μ is the gyromagnetic ratio of μ^+ and γ_N is the nuclear gyromagnetic ratio of ^1H .

Then, we fit the ZF spectrum by Eq. (1) but using $P_{\text{H}\mu}(t)$ or $P_{\text{H}\mu\text{H}}(t)$ instead of $G^{\text{tri}}(t)$ (see Fig. 8). Table III summarizes the parameters obtained by fit of the ZF spectrum using the three functions. It is clear that the fit using $G^{\text{tri}}(t)$ provides the best result among the three. Although the fit using $P_{\text{H}\mu}(t)$ provides the second best result, A_m is larger than A_{KT} . Moreover, since $\nu \gg \Delta$, the KT signal shows an exponentially relaxing behavior. As a result, the fit using the $P_{\text{H}\mu}(t)$ signal does not reproduce the second maximum at $t \sim 11 \mu\text{s}$ in the ZF spectrum. This suggests that the implanted muons prefer to locate close to H_2O to form $[\text{H}_2\mu\text{O}]^+$ rather than substituting (or ejecting) H^+ to make $\text{H}\mu\text{O}$. In addition, the absence of OH^- anions in the sample⁵ excludes the formation of $\text{H}\mu\text{O}$ through the direct bond between μ^+ and OH^- . For the fit using $P_{\text{H}\mu\text{H}}(t)$, the Gaussian relaxation (σ) of the $P_{\text{H}\mu\text{H}}(t)$ signal is eventually 0, suggesting that the result is not reliable. Therefore, the formation of oxoniumlike $[\text{H}_2\mu\text{O}]^+$ ions is the most reasonable explanation for the oscillatory signal in the ZF spectra for the H_2O intercalated samples.

Following upon the fit of the ZF spectrum, we consider the muon sites responsible for the oscillatory signal. Figure 9 shows the crystal structure of $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{D}_2\text{O}$ determined by neutron scattering.⁴¹ The occupancy for each D site is 0.6, that for the Na1 is 0.21, and that for the Na2 site is 0.14. According to Table III, $2d=3.42 \text{ \AA}$ for the $P_{\text{H}\mu\text{H}}$ signal. This roughly corresponds to the distance between the two H^+ ions above and below Na plane, which is represented by a narrow arrow. This suggests that the muons responsible for the oscillatory signal locate at interstitial sites in the Na

TABLE III. μ^+ SR parameters estimated from the fit of the ZF spectrum at 1.4 K for the H_2O intercalated SCII sample. We used three different fit functions; that is, a combination of the KT signal, $P_{\text{H}\mu}$ ($P_{\text{H}\mu\text{H}}$ or G^{tri}) signal, and BG signal. For the G^{tri} signal case, the fit function is equivalent to Eq. (1). A_m corresponds to the asymmetry of the $P_{\text{H}\mu}(t)$, $P_{\text{H}\mu\text{H}}(t)$, or $G^{\text{tri}}(t)$ signal.

Function	A_{KT}	A_m	A_{BG}	$d_{\text{H}-\mu}$ ($\text{\AA}$)	σ (10^6 s^{-1})	χ^2/N
$P_{\text{H}\mu}$	0.1000 ± 0.0007^a	0.1624 ± 0.0007	0.0197 ± 0.0005	1.597 ± 0.002	0.207 ± 0.002	1.216
$P_{\text{H}\mu\text{H}}$	0.2127 ± 0.0006^b	0.0291 ± 0.0008	0.0396 ± 0.0004	1.711 ± 0.006	0.00006 ± 0.17	1.359
G^{tri}	0.1800 ± 0.0004^c	0.0385 ± 0.0005	0.0627 ± 0.0004	1.712 ± 0.003	0.100 ± 0.005	1.075

^a $\Delta = (0.464 \pm 0.014) \times 10^6 \text{ s}^{-1}$ and $\nu = (8.27 \pm 0.18) \times 10^6 \text{ s}^{-1}$.

^b $\Delta = (0.405 \pm 0.002) \times 10^6 \text{ s}^{-1}$ and $\nu = (0.212 \pm 0.006) \times 10^6 \text{ s}^{-1}$.

^c $\Delta = (0.423 \pm 0.002) \times 10^6 \text{ s}^{-1}$ and $\nu = (0.213 \pm 0.005) \times 10^6 \text{ s}^{-1}$.

FIG. 9. (Color online) Crystal structure of $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{D}_2\text{O}$ determined by neutron scattering (Ref. 41). A green arrow represents a proper distance ($2d=3.269$ Å) for explaining the oscillation in the ZF spectrum by the H- μ -H system.

plane. However, such site is electrostatically unstable because the Na ions locate only at the Na1 site (0, 0, 1/4) and Na2 site (1/3, 2/3, 1/4) in the Na plane. On the contrary, assuming that muons locate at the vacant Na1 site, the distance to the nearest neighboring H ($d_{\text{Na1-H}}^{\text{NN}}$) is 1.62 Å. But, the angle between nearest neighbors ($\angle \text{HNa1H}$) is 67° , 100° , or 143° , being inconsistent with a colinear system. For the case that muons locate at the vacant Na2 site, $d_{\text{Na2-H}}^{\text{NN}}$

$=2.602$ Å and it is too long for explaining the oscillation by the $P_{\text{H}\mu\text{H}}$ signal.

Consequently, combining the fit result with the crystallographic consideration, the muons responsible for the oscillatory signal are assigned to locate at the vacant H (D) sites, resulting in the formation of oxoniumlike $\text{H}_2\mu\text{O}(\text{D}_2\mu\text{O})$ ions. This is consistent with the fact that both the oscillation frequency [$k/(2\pi)$] and its relaxation rate ($\sigma_{\text{H}_2\mu\text{O}}$) are almost T independent between 1.8 and 100 K [see Figs. 4(b) and 4(c)]. If the muon and H are part of different molecules, thermal expansion and vibration will probably change the mean distance. However, majority of the implanted muons are likely bound to an O^{2-} in the CoO_2 plane to form $[\text{O}\mu]^-$ or occupy some interstitial sites, neither of which give the characteristic oscillations, but a KT behavior. In fact, when muons locate in the vicinity of the O^{2-} ions of the CoO_2 plane but ~ 1 Å away along the c axis, which is a typical muon site for the layered transition-metal dioxides,^{34,35,45–47} the distance to the nearest-neighboring H is 0.86 Å and that to the second nearest-neighboring H is 2.2 Å. The two distances are very different from $d_{\text{H-}\mu}^{\text{NN}} (=1.597$ nm) estimated from the fit using the $P_{\text{H}\mu}(t)$ signal, as expected.

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