Abstract

In order to clarify the carrier density dependence of the microscopic magnetic nature in NaₓCoO₂ × yH₂O, we have performed a μ⁺SR study of H₂O and D₂O absorbed samples. Based on the ZF-μ⁺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 Tc. Furthermore, the ZF-spectrum for the H₂O absorbed sample exhibits a clear oscillation in the whole T range measured (1.4-100 K), suggesting the formation of “[H₃O]⁺-like” H₂μ⁺O ions in the sample. The absence of the oscillation in the D₂O absorbed sample also evidences the presence of the H₂μ⁺O complex. Considering the fraction of the H₂μ⁺O signal, we have demonstrated the coexistence of [H₃O]⁺ ions and H₂O in this compound. Finally, the muonic Knight shift measurements suggested the change in electronic state around 10 K and 40 K for the SCI and SCII samples.

Keywords: Superconductivity phase diagrams, Superconducting materials other than cuprates, Spin glasses and other random magnets, Chemical and Knight shifts, Muon-spin rotation and relaxation
Figure 1: (a) The magnetic phase diagram of hexagonal Na$_{0.35}$CoO$_2$·1.3H$_2$O determined by $^{59}$Co NQR and susceptibility measurements [13], (b) the ZF-$\mu^+$SR spectra for the H$_2$O and D$_2$O intercalated SCII samples obtained in ISIS, (c) the $T$ dependence of the field distribution width ($\Delta$) for the H$_2$O intercalated samples, and (d) those for the D$_2$O intercalated samples. In (a), open circles represent the H$_2$O intercalated samples used for the present $\mu^+$SR study and open triangles the D$_2$O intercalated samples. The present M samples did not exhibit a superconducting transition down to the lowest $T$ measured (1.8 K). In (b), the solid lines represent the fit results using the combination of the H$_2$O signal, a Kubo-Toyabe signal, and an off-set signal for the H$_2$O intercalated samples, whereas using a Gaussian relaxing cosine oscillation signal instead of the H$_2$O signal for the D$_2$O intercalated samples [22]. $\Delta$ in (c) and (d) was obtained by fitting the ZF-spectrum. The estimated error of $\Delta$ was below the symbol size.

Recently, Ohta et al. found a route to control the carrier density of the CoO$_2$ plane by keeping the Na$_x$(H$_3$O)$_z$CoO$_2$·yH$_2$O sample in a humid atmosphere [8] for different amount of time. The electronic and magnetic phase diagram of Na$_x$CoO$_2$·yH$_2$O ($x \sim 0.35$, $y \sim 1.3$) was subsequently clarified by both nuclear quadrupole resonance (NQR) and magnetic susceptibility ($\chi$) measurements (see Fig. 1) [9, 10, 11, 12, 13]. That is, as the $^{59}$Co-NQR frequency ($\nu_{Q3}$) 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 $\nu_{Q3}$ 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 $\nu_{Q3} = 12.74$ MHz (see Fig. 1). Here, $\nu_{Q3}$ is proportional to the distortion of the CoO$_6$ octahedron, and as a result, $\nu_{Q3}$ 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, 17, 18, 19, 20, 21].

We have, therefore, carried out a systematic $\mu^+$SR study for the three phases using both H$_2$O and D$_2$O intercalated samples. Particularly, since the spin angular momentum of D is unity while that of H is $1/2$ and the nuclear magnetic moment of D is much smaller than that of H, we could obtain a clear insight on the magnetic nature of the water intercalated Na$_x$CoO$_2$, by the comparison of the results between H$_2$O and D$_2$O intercalated samples. Here, we demonstrate the direct evidence for the coexistence of [H$_3$O]$^+$ and H$_2$O and the absence of any crucial difference in the microscopic magnetic nature between the SCI and SCII phase.

2. Experiment

The Na$_x$(H$_3$O)$_z$CoO$_2$·yH$_2$O and Na$_x$(D$_3$O)$_z$CoO$_2$·yD$_2$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 Na$_x$(H$_3$O)$_z$CoO$_2$·yH$_2$O or Na$_x$(D$_3$O)$_z$CoO$_2$·yD$_2$O by powder X-ray diffraction. Prior to $\mu^+$SR measurements, their magnetization was measured by a SQUID magnetometer with magnetic field $H = 20$ Oe. Their $^{59}$Co-NQR spectrum was also measured to estimate $T_c$ and the NQR frequency $\nu_{Q3}$. Typical results are shown in Fig. 1(a). All the samples used for the $\mu^+$SR measurements were confirmed to obey the phase diagram; that is, open circles for the H$_2$O intercalated samples and open triangles for the D$_2$O 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 $\mu^+$SR facility in a cool box. The $\mu^+$SR
spectra were measured at the surface muon beam lines using the MuSR spectrometer in ISIS. In addition, TF-$\mu^+$SR spectra were obtained with $H_{TF} = 20$ kOe using the Helios spectrometer in TRIUMF.

### 3. Results and Discussion

Figure 1(b) shows the ZF-$\mu^+$SR spectra for the two water-intercalated samples, i.e., the H$_2$O and D$_2$O intercalated SCII samples. Both 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, $^1$H and $^2$H (= D). In addition, the ZF-spectra for the H$_2$O intercalated samples exhibit a clear oscillation with a small amplitude ($\sim 0.02$). Since the initial asymmetry ($A_0$) is the maximum value for the present setup ($\sim 0.28$) 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$_2$O samples. This clearly demonstrates the appearance of an internal magnetic field ($T_S = \chi$)

$T_S$ value for the present setup ($\sim 28$) for all the ZF-spectra and the overall relaxation is described well by a KT behavior, indicating a superconducting behavior

$\Delta T_c$ decreases from 50 K, $\Delta$ for the H$_2$O intercalated M samples remains at the same value as the SC samples down to 6 K, and then, $\Delta$ 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 the field fluctuation rate ($v$) is $T$-independent regardless of $T_m$. Since the volume fraction of the H$_2\mu^+$O signal ranges between 0.22 and 0.27, the majority of the implanted muons feel the random nuclear magnetic field — i.e. the KT field distribution. Therefore, it is difficult to determine the muon sites correctly. But, the muons responsible for the H$_2\mu^+$O signal naturally locates near H$_2$O so as to make a $\mu^+$-O bond. In fact, based on the oscillation frequency of the H$_2\mu^+$O signal, the $\mu^+$-O bond length is estimated as $\sim 1.76$ Å for the three H$_2$O intercalated samples. This is comparable to the the edge length of the regular triangle of the H ions in the oxonium ion (1.6296 Å).

Then, we have moved to the Knight shift ($K$) measurements to further elucidate the difference among the three phases. In order to estimate $f_{TF}$ precisely, the TF-spectra from the sample and reference (Ag) were fitted simultaneously to a power exponentially relaxing cosine oscillation (using a rotating frame analysis) [24],

$$A_0^N P_{TF}^N(t) = A_{TF}^N \cos(\omega_{TF}^N t + \phi^N) \times \exp(-\lambda_{TF}^N t^\beta)$$

where $A_{TF}$ is the asymmetry, $\omega_{TF}$ is the muon Larmor frequency of the oscillating signal ($\omega_{TF}^N \equiv 2\pi \times f_{TF}^N$), $\phi$ is the initial phase of the precession, $\lambda_{TF}$ is the exponential relaxation rate, and $\beta$ is the power. The superscript $N$ (= S or R) represents the signal from the sample or reference. $K$ is defined by $K \equiv (\omega_{TF}^S - \omega_{TF}^R)/\omega_{TF}^R$.

Figure 2 shows the $\chi(T)$, $K(T)$, $K(\chi)$, and $A_{HF}(T)=K/\chi$ curves for the H$_2$O intercalated SCII sample. The $\chi(T)$ curve for the SCI sample exhibits a change in the slope at $T_c$, indicating a superconducting behavior even under $H = 20$ kOe, as expected. On the other hand, such change is very ambiguous in the $\chi(T)$ curve for the SCII sample. However, there are no crucial differences among the TF-$\mu^+$SR data of the three samples in the whole $T$ range measured. Here, a hyperfine coupling constant at the muon sites ($A_{HF}$) was estimated from the relationship between $K$ and $\chi$ [Fig. 2(d)].
Figure 2: (color online) (a) T dependence of susceptibility (χ), (b) T dependence of muonic Knight shift (K), (c) the relationship between K and χ, and (d) T dependence of hyperfine coupling constant $A_{hf}$ for the H$_2$O absorbed SCI, M, and SCII samples. χ was measured in field cooling mode with $H = 20$ kOe. The $μ^+SR$ data were obtained by fitting the TF-spectra measured with $H = 20$ kOe using Eq. (1).

As seen in Fig. 2(c), the change in the slope of the $K(χ)$ curve around 10 K suggests the change in the electronic state of the CoO$_2$ plane for all the three samples. Only for the SCI sample, as T further decreases from 10 K, $A_{hf}$ levels off to $\sim -3.5$ kOe/$μ_B$ below 5 K due to the change in χ caused by superconductivity. Note that the present $A_{hf}$ is about 10 times larger than the reported $A_{hf}$ measured with $H_{TF} = 60$ kOe [25], for reasons currently unknown. Since $H_{TF} = 20$ kOe $< H_c2$, we naturally concentrate the TF-$μ^+SR$ parameters in a paramagnetic state above $T_c$. Interestingly, the slope of the $K(χ)$ curve for each sample becomes smaller again above $\sim 40$ K, indicating a further change in the electronic state around 40 K. Therefore, it is highly preferable to use the $K(T)$ data below 10 K to discuss the nature of the SCI, M, and SCII phase.

In summary, 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, a random and small magnetic field was detected below $T_m$ both for the H$_2$O and D$_2$O intercalated samples. Furthermore, we found a clear oscillation in the ZF-spectra only for the H$_2$O intercalated samples, but no oscillations for the D$_2$O intercalated samples. According to numerical analyses of the ZF-spectra, the origin of the oscillation was clarified as the formation of “[H$_3$O]$^+$-like” H$_2$$\mu$+$O$ ions. Finally, the muonic Knight shift measurements suggested the change in electronic state around 10 and 40 K for all the three H$_2$O intercalated samples.

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