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Possible unconventional superconductivity and weak magnetism in $Na_xCoO_2 \cdot yH_2O$ probed by μSR

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Abstract

The superconducting property of sodium cobalt oxyhydrate, $Na_{0.35}CoO_2 \cdot 1.3H_2O$, has been studied by means of muon spin relaxation (μSR) down to 2 K. It was found that the zero-field muon spin relaxation rate is independent of temperature, indicating that no static magnetism appears in this compound above 2 K. The result also provides evidence against the breakdown of time-reversal symmetry for the superconducting order parameter. In water excess sample $Na_{0.334}CoO_2 \cdot 1.32H_2O$, which shows no superconductivity, the weak magnetism was observed below 6 K. This fact suggests that the magnetic interaction plays an important role for the appearance of the unconventional superconductivity.

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Keywords: $Na_{0.35}CoO_2 \cdot 1.3H_2O$; μSR; Superconductivity; Magnetism

1. Introduction

The recent discovery of superconductivity in a novel cobalt oxide, $Na_xCoO_2 \cdot yH_2O$ ($x = 0.35$, $y = 1.3$), with the transition temperature $T_c \sim 5$ K, is attracting much interest [1]. The compound has a lamellar structure consisting of CoO_2, Na and H_2O layers, where the two-dimensional (2D) CoO_2 layers are separated by thick insulating Na or H_2O 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 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 CoO_2 layers, where a strong magnetic frustration is anticipated. Thus, while $Na_{0.35}CoO_2 \cdot 1.3H_2O$ may be viewed as an electron-doped Mott insulator for a low-spin 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 [2–8], 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 [9], the $d_{x^2-y^2} + id_{xy}$ state [10–13], and the f state [14] are argued. It is notable that some of these states break the time-reversal symmetry of the Cooper pairs,

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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-μSR) technique.

In this article, we report on the magnetic and superconducting properties of $Na_{0.35}CoO_2 \cdot 1.3H_2O$ studied by means of the muon spin rotation/relaxation method (μSR) down to 2 K. It is inferred from the ZF-μSR 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. We also report the magnetism in the water excess specimen $Na_{0.334}CoO_2 \cdot 1.32H_2O$ which shows no superconductivity.

2. Experimental

Powder specimens of $Na_{0.35}CoO_2 \cdot 1.3H_2O$ and $Na_{0.334}CoO_2 \cdot 1.32H_2O$ were synthesized, as described in Ref. [1]. We used two different batches of $Na_{0.35}CoO_2 \cdot 1.3H_2O$ with same T_c (~4.5 K) for ZF-μSR. Each specimen was characterized by measuring the magnetic susceptibility prior to a μSR measurement. Conventional μSR measurement under zero field was carried out at the πA-port of the Muon Science Laboratory, High Energy Accelerator Research Organization (KEK). 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 ~100 K to preserve its water content. For ZF-μSR, residual field was reduced to below 10 mOe by using three pairs of correction magnets.

3. Results and discussions

Fig. 1 shows the time evolution of the muon spin polarization in $Na_{0.35}CoO_2 \cdot 1.3H_2O$ at 10 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, $G_{KT}(\Delta, \nu, t)$[15], as indicated by the solid line in Fig. 1. Here, Δ/γ_μ is the second moment of the field distribution at the muon site, with γ_μ being the muon gyromagnetic ratio ($= 2\pi \times 13.55$ kHz/Oe), and ν is a fluctuation rate of the nuclear dipolar field. From a fitting analysis, we obtained $\Delta/\gamma_\mu \sim 5.0$ Oe and $\nu \sim 0.22\,\mu s^{-1}$ at 10 K. The origin of this fluctuation is not known and it might be from the motion of water molecules. By comparing the experimental value of Δ in the normal phase (10 K) of $Na_{0.35}CoO_2 \cdot 1.3H_2O$ ($\Delta = 0.425(4)\,\mu s^{-1}$) and that in the deuterated specimen ($\Delta = 0.243(3)\,\mu s^{-1}$) [16] together with calculated mapping of Δ, the muon-stopping site was identified around (0.2, 0.25, 0.12) which is between CoO_2 layer and a water molecule.

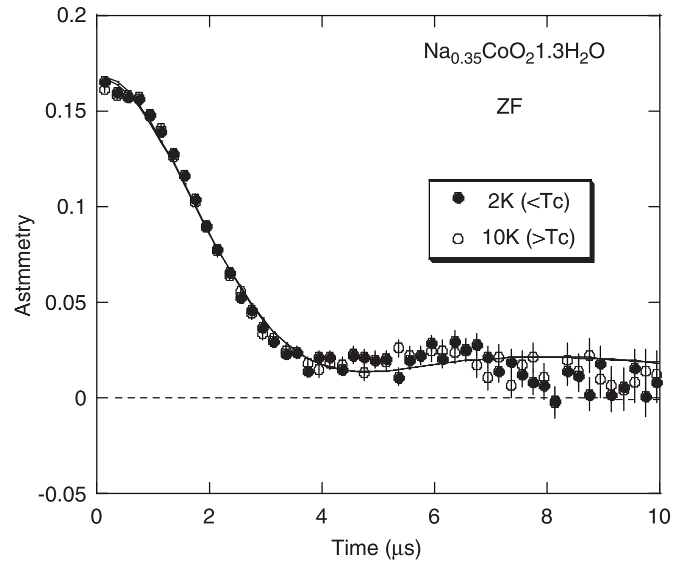

Fig. 1. Zero-field μSR spectra of $Na_{0.35}CoO_2 \cdot 1.3H_2O$ at 10 K (normal phase) and 2 K (superconducting phase).

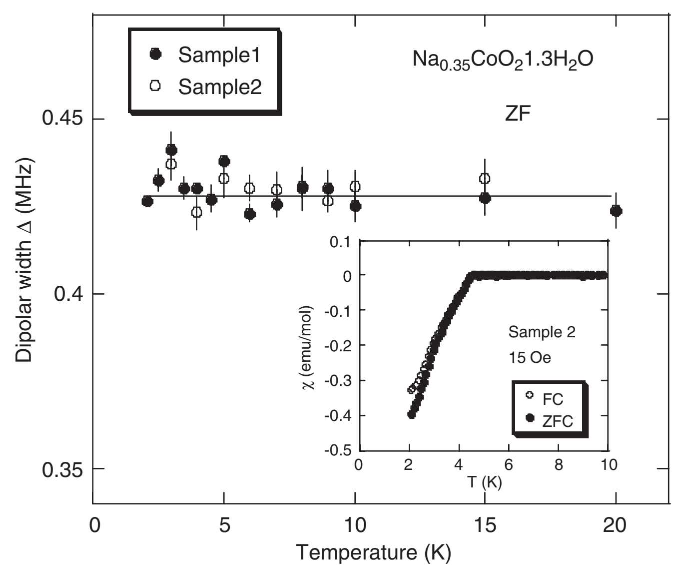

Fig. 2. Temperature dependence of the dipolar width in $Na_{0.35}CoO_2 \cdot 1.3H_2O$. Inset shows the temperature dependence of the magnetic susceptibility.

As evident in Fig. 1, we observed no significant change in the ZF-μSR time spectrum while the temperature passed T_c. Fig. 2 shows the temperature dependence of the dipolar width (Δ), 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 μSR (10^{-9}–10^{-5} s). The upper bound for the possible magnetic moment was estimated to be $0.002\mu_B$/Co in $Na_{0.35}CoO_2 \cdot 1.3H_2O$ by using the hyperfine coupling constant, $A_{hf} = -0.20\,kOe/\mu_B$ [16]. Similar ZF-μSR result was obtained by Uemura et al. [17].

It is theoretically suggested that spontaneous magnetic fields are induced below the superconducting transition