23Na NMR Study of Layered Superconductor NaₙCoO₂ · yH₂O

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Abstract

We measured 23Na-NMR spectra and nuclear spin-lattice relaxation rates 23(1/T₁) of superconducting and non-superconducting bilayer hydrate NaₙCoO₂ · yH₂O (x ≈ 0.3, y ≈ 1.3). The central resonance frequency shows a small but various shift due to the difference in the shielding effect by intercalated H₂O molecules. The different shielding effect also gives a large difference in the magnitude of 23(1/T₁).

Key words: Sodium cobalt oxide, Superconductivity, 23Na-NMR
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Recently, a number of investigations for the superconductivity in bilayer hydrate (BLH) sodium cobalt oxide NaₙCoO₂ · yH₂O (x ≈ 0.3, y ≈ 1.3) have been done. Different properties were reported especially in NMR studies for different samples. In a report of chemical study, it is emphasized that some Na⁺ ions are exchanged by H₃O⁺ ions during intercalation of H₂O molecules[1]. Because of the nonstoichiometric properties in BLH, i.e. ambiguities of the amount of Na⁺, H₂O, and H₃O⁺, similar samples are hardly obtained. More chemical studies are needed to clarify the origin of the magnetism and the superconductivity of BLH.

We prepared two BLH samples by following processes[2]. Powders of Co₃O₄ and Na₂CO₃ were well mixed and heated at 800 °C for 20 hours in O₂ atmosphere. The obtained powder sample was characterized as in a single phase of Na₀.₇CoO₂ by powder X-ray diffraction (XRD) measurements. Then Na₀.₇CoO₂ was immersed in Br₂/CH₃CN solution for several days to deintercalate Na ions. The dried powder was immersed in distilled water for 1 day. The water-intercalated powder was put in a sealed chamber filled with 75 % of relative humidity (RH). We prepared several samples by changing the duration kept in the chamber, and frozen at about -10 °C for quenching further change. A sample named BLH1 was kept for one week in 75 % RH atmosphere, and BLH2 for 1 month.

Another two samples named BLHs1 and BLHs2 were synthesized by similar process, but not at the same time with BLH1 and BLH2. BLHs1 has already been studied in [3]. BLHs2 was a derivative of BLHs1 after about 1 year in the 75 % RH atmosphere before frozen.

Each sample was characterized to be in a single phase of the BLH by powder XRD result. The lattice constant c of BLHs1 and BLHs2 estimated by the XRD results are smaller than that of BLH1 and BLH2. This difference in c indicates that the content of H₃O⁺ is different between two groups. The superconducting transition temperature Tc estimated by magnetization measurements was Tc < 1.8 K for BLH1 and ~4.5 K for BLH2; Tc ~ 4.7 K for BLH1 and ~3 K for BLHs2.

We observed the free induction decay (FID) signals of 23Na nuclei (I = 3/2) by NMR at 7.485 T. The Fourier transformed NMR spectra of FID signals are shown in Fig. 1. Here, νrel denotes the resonance fre-
frequency of $^{23}$Na nuclei in NaCl aqueous solution at room temperature ($\nu_{\text{ref}} = 84.287$ MHz). The satellite lines due to the nuclear quadrupole interaction may wipe out. The shift of peak resonance is very small compared with Na$_2$CoO$_2$ ($\nu - \nu_{\text{ref}} \sim 40$ kHz)[4], and the temperature dependence of the shift is also small, suggesting a weak Co-O-Na coupling.

The hyperfine coupling is thought to be $\sim 0.05$ kHz. The hyperfine coupling of BLH is on two or three order smaller than that of $^{23}$Na nuclei[5]. Since $1/T_1$ becomes slower with increasing the duration, the shielding effect is enhanced by the time duration in the chamber. We note that the different surroundings around a sodium ion. Since $1/T_1$ becomes slower with increasing the duration, the shielding effect is enhanced by the time duration in the chamber. We note that the different surroundings around a sodium ion. Since $1/T_1$ becomes slower with increasing the duration, the shielding effect is enhanced by the time duration in the chamber.

The recovery curves of FID signals were measured by inversion recovery method for obtaining $^{23}$Na nuclear spin-lattice relaxation rate $^{23}(1/T_1)$. The temperature dependence of $^{23}(1/T_1)$ is shown in Fig. 2. The relaxation rate was estimated by the least-square fitting using the theoretical function of the central transition ($I_z = 1/2 \leftrightarrow -1/2$). While the peak shift is small and similar in each BLH as shown in Fig. 1, the absolute value of $^{23}(1/T_1)$ is markedly different. A broad peak around $100 \sim 150$ K in each $^{23}(1/T_1)$ and a rapid increase above $200$ K except for BLHs2 are observed. This rapid increase in $^{23}(1/T_1)$ may originate in the motion of Na ions[5].

The magnitude of $^{23}(1/T_1)$ of BLH is on two or three order smaller than that of Na$_2$CoO$_2$[5,6]. If the hyperfine coupling of BLH is on two or three order smaller than that of Na$_2$CoO$_2$, the shift should be $0.05 \sim 0.5$ kHz. The hyperfine coupling is thought to be shielded by the intercalated H$_2$O molecules. The difference in $^{23}(1/T_1)$ may be attributed to the difference of compositions of H$_2$O, H$_2$O$^+$, and Na$^+$, which may cause the different surroundings around a sodium ion. Since $1/T_1$ becomes slower with increasing the duration, the shielding effect is enhanced by the time duration in the chamber. We note that $^{59}$Co and $^{17}$O-NMR/NQR are hard to probe these difference of compositions, because Co and O nuclei are in the CoO$_2$ plane and outside of the layer consisting of the nonstoichiometric components. Therefore, $^{23}$Na-NMR should be a strong probe to elucidate the physical properties of the BLH.

In conclusion, we measured $^{23}$Na-NMR in bilayer hydrate sodium cobalt oxides, including nonsuperconducting bilayer hydrate. At the Na site, the hyperfine coupling is weakened by the intercalated H$_2$O molecules, and the nuclear spin-lattice relaxation shows a large difference in four samples with different superconducting temperatures.

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