59Co-NMR Knight Shift of Superconducting Three-Layer Na4CoO2yH2O

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The superconducting state of Na4CoO2yH2O with three CoO2 layers in a unit cell has been studied by 59Co-NMR

The Knight shift measured for a peak of the NMR spectra corresponding to the external magnetic field $H$ along one of the principal directions within the CoO2 plane, exhibits a rapid decrease with decreasing temperature $T$ below the superconducting transition temperature $T_c$, indicating that the spin susceptibility $\chi_{\text{spin}}$ is suppressed in the superconducting phase, at least, for this field direction. Because differences of the superconducting properties are rather small between this three-layer Na4CoO2yH2O and previously reported Na4CoO2yH2O with two CoO2 layers within a unit cell, the present result of the Knight shift studies indicates that the Cooper pairs of the former system are in the singlet state as in the latter, for which the spin susceptibility is suppressed for both directions of $H$ parallel and perpendicular to the CoO2 plane.

KEYWORDS: Na4CoO2yH2O, Superconductivity, 59Co-NMR, Knight shift

1. Introduction

The hydrated Co oxide Na4CoO2yH2O (x~0.3 and y~1.3) having two CoO2 layers within a unit cell, which are formed of edge-sharing CoO6 octahedra exhibits the superconducting transition at temperature $T = T_c$~4.5 K.1) Because the layers have the triangular lattice of Co atoms, roles of the geometrical frustration are, naïvely speaking, expected to be important for the occurrence of the superconductivity, and much attention has been paid to the system. It is also presumed that strong spin excitations are related to the superconductivity, because the spin state change is often found in Co3+ ions in various kinds of Co oxides.2,4) Then possible exotic characters have been intensively pursued and the pairing symmetry is being hotly argued.5,12)

We have studied the 59Co-NMR Knight shift $K$ of two-layer Na4CoO2yH2O5,7) and reported that it decreases with decreasing $T$ below $T_c$ for both directions of the applied field $H$ within the ab-plane and parallel to the c-axis.5) The result indicates that the superconducting electron pairs are in the singlet state.

In this paper, results of the 59Co-NMR studies on another superconducting system of Na4CoO2yH2O13,15) which has three layers of edge-sharing CoO6 octahedra within a unit cell, are presented. The $T_c$ value of this three-layer Na4CoO2yH2O is ~4.5 K, nearly equal to that of two-layer Na4CoO2yH2O.

In Fig. 1, the structures of (a) P2-Na0.75CoO2 and (b) O3-NaCoO216,17) are compared. In the figure, we can recognize that the repetition of the layer sequences of (Co$_{\text{ox}}$,Na,Co$_{\text{Oy}}$,Na,Co$_{\text{Oz}}$,Na) and (O$_{\text{xy}}$Co$_{\text{Oy}}$,Na,Co$_{\text{Oz}}$,Na,Co$_{\text{Oz}}$,Na,Co$_{\text{Oy}}$,Na) within a unit cell are repeated, for P2-Na0.75CoO2 and (b) O3-NaCoO2, respectively, where Ox (X=A, B, A’, B’ and C’) distinguish the oxygen layers. The superconducting systems are prepared by de-intercalating Na atoms and then, intercalating H2O molecules. During these processes, the stacking sequence of P2-Na0.75CoO2 is kept unchanged, while the O3-NaCoO2 is transformed to the P3 type one with a sequence of (-O$_{\text{xy}}$,Co$_{\text{Oy}}$-Na$_{\text{Oz}}$-Co$_{\text{Oz}}$-Na$_{\text{Oy}}$-Co$_{\text{Oy}}$-Co$_{\text{Oz}}$-Na$_{\text{Oz}}$-Na).15)

We have performed 59Co-NMR studies of the powder samples of P3-Na4CoO2yH2O and compared the observed results with those of P2-Na4CoO2yH2O.

Fig. 1. Crystal structures of (a) P2-Na0.75CoO2 and (b) O3-NaCoO2; where the Na sites are shown by the dark spheres and Co sites are within the shaded octahedra formed of the corner oxygens. In O3-NaCoO2, the Na sites are fully occupied, while in P2-Na4CoO2, there are two crystallographically distinct Na sites with different occupancies.

2. Syntheses and Characterizations of the samples

Powder samples of P3-Na4CoO2yH2O were synthesized by using the procedure described in ref. 13: The mother system O3-NaCoO2 was synthesized, by heating NaOH pellets buried in the powder of Co metal in air at 500 °C for 12 h, where we had to use the 25 % excess amount of NaOH to obtain O3-phase samples of NaCoO2. If the molar ratio of Na and Co is smaller than ~1.25, a significant amount of P2-Na4CoO2 with
Finally, in order to obtain the superconducting hydrated phase 
$P_2$-Na$\cdot$CoO$_2$$\cdot$yH$_2$O, the obtained powder sample of 
$P_2$-Na$\cdot$CoO$_2$$\cdot$yH$_2$O was sealed in a chamber with 
H$_2$O vapor at room temperature for a week. The powder 
was immersed in the 13-15) octahedra in $P_2$- and $P_3$-Na$\cdot$CoO$_2$$\cdot$yH$_2$O are almost equal. We can expect that the principal axis $z$ of the latter system is parallel to the $c$ axis, as in $P_2$-Na$\cdot$CoO$_2$$\cdot$yH$_2$O. The peak indicated by the arrow in Fig. 4 corresponds to the magnetic field direction parallel to one of the principal directions ($y$-direction) within the $ab$-plane. We have measured the $T$-dependence of this peak at frequencies $f = 23.566, 33.281$ and 43.625 MHz. The value of the resonance field $H_{\text{res}}$ determined as the peak position of the magnetic field $H$ begins to exhibit rather rapid increase with decreasing $T$ at the transition temperature $T_c$ for all frequencies. This behavior is similar to that of $P_2$-Na$\cdot$CoO$_2$$\cdot$yH$_2$O. For example, the peak profiles observed at various temperatures for $f = 23.566$ MHz are shown in Fig. 5, where the peak values are

$\chi_{\text{observed}}$ is about 4.5 K, which is nearly equal to that of $P_2$-Na$\cdot$CoO$_2$$\cdot$yH$_2$O.

$\chi_{\text{calculated}}$ is about 4.5 K, which is nearly equal to that of $P_2$- and $P_3$-Na$\cdot$CoO$_2$$\cdot$yH$_2$O.

$\chi$ vs $T$ for $P_3$-Na$\cdot$CoO$_2$$\cdot$yH$_2$O measured with the magnetic field $H = 5$ Oe.

$^{59}$Co-NMR spectra were obtained for the randomly oriented powder sample of $P_3$-Na$\cdot$CoO$_2$$\cdot$yH$_2$O by the spin-echo technique using a phase coherent type pulse spectrometer. The echo intensity was recorded with the applied magnetic field changed stepwise. The nuclear longitudinal relaxation rate $1/T_1$ of $^{59}$Co nuclei was measured by measuring the $^{59}$Co nuclear magnetization $m$ as a function of the time $t$ elapsed after applying an inversion pulse in the frequency region around $3\nu_0$, $\nu_0$ being the electrical quadrupolar frequency (~4 MHz). The $\{1-m(t)/m(\infty)\}$-$t$ curves were found to be described by the theoretical one. Other details can be found in ref. 6.

3. Results of the NMR Studies and Discussion

Field swept spectra of $^{59}$Co NMR taken at 5 K with the frequency $f = 23.566$ MHz are shown in Fig. 4 together with the result of the model calculation (broken line) obtained as described in ref. 6 for $P_2$-Na$\cdot$CoO$_2$$\cdot$yH$_2$O. In the present case, the used NMR parameters are as follows. The quadrupolar frequency $\nu_Q$ is 4.1 MHz, the Knight shifts $K_x = 3.2\%$, $K_y = 3.5\%$ and $K_z = 2.1\%$ for locally defined principal axes at Co sites, $x$, $y$ and $z$, respectively and the asymmetric parameter $\eta = 0.3$. These parameters, which can well reproduce the observed spectra, are rather similar to those obtained for $P_2$-Na$\cdot$CoO$_2$$\cdot$yH$_2$O. Because the trigonal distortions of CoO$_6$ octahedra in $P_2$- and $P_3$-Na$\cdot$CoO$_2$$\cdot$yH$_2$O are almost equal, we can expect that the principal axis $z$ of the latter system is parallel to the $c$ axis, as in $P_2$-Na$\cdot$CoO$_2$$\cdot$yH$_2$O. The peak indicated by the arrow in Fig. 4 corresponds to the magnetic field direction parallel to one of the principal directions ($y$-direction) within the $ab$-plane. We have measured the $T$-dependence of this peak at frequencies $f = 23.566, 33.281$ and 43.625 MHz. The value of the resonance field $H_{\text{res}}$, determined as the peak position of the magnetic field $H$ begins to exhibit rather rapid increase with decreasing $T$ at the transition temperature $T_c$ for all frequencies. This behavior is similar to that of $P_2$-Na$\cdot$CoO$_2$$\cdot$yH$_2$O. For example, the peak profiles observed at various temperatures for $f = 23.566$ MHz are shown in Fig. 5, where the peak values are

![Fig. 2. The X-ray powder diffraction patterns observed for the samples of (a) $P_2$- and (b) $P_3$-Na$\cdot$CoO$_2$$\cdot$yH$_2$O are compared with the integrated intensities calculated by using the space groups $P_6/mmc$ and $R\overline{3}m$, respectively. The data in the high angle regions are shown in Fig. 5, where the peak values are compared with the result of the model calculation (broken line) obtained as described in ref. 6 for $P_2$-Na$\cdot$CoO$_2$$\cdot$yH$_2$O.](image-url)
adjusted to that shown in Fig. 4 (in Fig. 5, almost the whole part of the profiles above the dip found at the higher field side of the peak is shown and the shift of the peak toward the higher field side with decreasing $T$ is evident). The shift occurs due to the magnetic shift and/or the effect of the second order and higher order $eqQ$ interactions. In the present case, it is considered that the magnetic shift predominantly contributes to the observed one, because the $T$ dependence of the shift originating from the quadrupolar interaction is considered to be negligibly small in this low temperature region.

In Fig. 6(a), the deviation of the resonance field $H_{\text{res}}$ from the value just above $T_c$, $\Delta H_{\text{res}}(T) = H_{\text{res}}(T) - H_{\text{res}}(T>T_c)$ observed for various frequencies (or various applied field) are shown. It is worth noting that at low temperatures the absolute value of $\Delta H_{\text{res}}$ increases with increasing $H$, which was also observed for P2-Na$_x$CoO$_2$yH$_2$O. This field dependence of $\Delta H_{\text{res}}$ cannot be explained solely by the superconducting diamagnetism $M_{\text{dia}}$ because the absolute value of $M_{\text{dia}}$ decreases with increasing $H$ in the measured $H$ region ($H >>$ the lower critical field $H_c$). Consequently, we can say that for the nonzero $\Delta H_{\text{res}}$ observed below $T_c$, the reduction of the spin magnetization $M_{\text{spin}}$ is important. (The orbital contribution to the Knight shift can be considered to be $T$ independent in this low temperature region.)

Figure 6(b) shows the $T$-dependence of $\Delta K(T) = f[\gamma_N H_{\text{ref}}(T)]/f[\gamma_N H_{\text{ref}}(T>T_c)]$ for various fixed frequencies, where $\gamma_N$ is the nuclear gyromagnetic ratio ($\gamma_N = 10.03$ MHz/T for $^{59}$Co). If we neglect the contribution of $M_{\text{dia}}$, the reduction of $\Delta K$ is due to the suppression of the spin component $K_{\text{spin}}$ of the Knight shift $K$. The magnitudes of $\Delta K$ for the present P3-Na$_x$CoO$_2$yH$_2$O are slightly smaller than those for P2-Na$_x$CoO$_2$yH$_2$O. 6,7 But, in both systems, $K_{\text{spin}}$ decreases below $T_c$, suggesting that the superconducting electron pairs should be considered to be in the singlet state, unless the spins of Cooper pairs in the triplet state are strongly

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**Fig. 4.** Field swept $^{59}$Co-NMR spectra of P3-Na$_x$CoO$_2$yH$_2$O taken at 5 K with a fixed frequency of 23.566 MHz for randomly oriented powder samples. The broken line shows the powder pattern calculated by the parameters $\nu_0 = 4.1$ MHz, $K_x = 3.2\%$, $K_y = 3.5\%$, $K_z = 2.1\%$ and $\eta = 0.3$.

**Fig. 5.** Temperature dependence of the profile of the peak indicated in Fig. 4 by the arrow is shown for a fixed frequency of 23.566 MHz. The solid lines are the guides for eyes.

**Fig. 6.** (a) Deviations of the resonance field from the value just above $T_c$, $\Delta H_{\text{res}}(T) = H_{\text{res}}(T) - H_{\text{res}}(T>T_c)$ are plotted against $T$ for $H || y$ at three fixed frequencies. (b) Deviations of the Knight shift from the value just above $T_c$, $\Delta K(T) = f[\gamma_N H_{\text{ref}}(T)]/f[\gamma_N H_{\text{ref}}(T>T_c)]$ are plotted against $T$ for various fixed frequencies, where $\gamma_N$ is the nuclear gyromagnetic ratio ($\gamma_N = 10.03$ MHz/T for $^{59}$Co).
pinned along the \( c \)-direction. On this point, we have already reported\(^7\) that in \( \mathrm{P}_2\text{-}\mathrm{Na}_{2}\text{CoO}_2\text{H}_2\text{O} \), \( \Delta K \) decreases (or \(|\Delta K|\) increases) with decreasing \( T \) below \( T_c \) for both directions of \( \mathbf{H} \) within the \( ab \)-plane and parallel to the \( c \)-axis. It indicates that the pairs are in the singlet state in \( \mathrm{P}_2\text{-}\mathrm{Na}_{2}\text{CoO}_2\text{H}_2\text{O} \).

Figure 7 shows the \( T \)-dependence of the upper critical field \( H_{c2} \) estimated from \( \Delta K(H,T) \) curves for \( \mathrm{P}_3\text{-}\mathrm{Na}_{2}\text{CoO}_2\text{H}_2\text{O} \), together with those of resistivity measurements for \( \mathrm{P}_2\text{-}\mathrm{Na}_{2}\text{CoO}_2\text{H}_2\text{O} \).\(^{16,21}\) The value of \( H_{c2}(T=0) \) is estimated to be about 8 T, which well agrees with the value expected from the Pauli paramagnetic limit \( H_p = 1.84T_c \) for systems with the negligible effect of the spin-orbit coupling and with \( T_c = 4.5 \) K. Because the Pauli limit arises from the pair breaking by the Zeeman effect, the observed value of \( H_{c2} \) implies that the singlet superconductivity is realized in the present cobalt oxide superconductor \( \mathrm{P}_3\text{-}\mathrm{Na}_{2}\text{CoO}_2\text{H}_2\text{O} \). Thus, we may consider that both of \( \mathrm{P}_2\text{-} \) and \( \mathrm{P}_3\text{-} \) \( \mathrm{Na}_{2}\text{CoO}_2\text{H}_2\text{O} \) possess the same superconducting pair symmetry. For \( \mathrm{P}_2\text{-}\mathrm{Na}_{2}\text{CoO}_2\text{H}_2\text{O} \), we have shown from the measurements of the Knight shifts that the spin susceptibility \( \chi_{\text{spin}} \) is suppressed for both directions of \( \mathbf{H} \) within and perpendicular to the \( ab \)-plane.\(^7\) For \( \mathrm{P}_3\text{-}\mathrm{Na}_{2}\text{CoO}_2\text{H}_2\text{O} \), we have not studied the shift for the perpendicular field, because it is difficult to grow single crystals of the mother system \( \mathrm{O}_3\text{-}\mathrm{Na}_{2}\text{CoO}_2\text{H}_2\text{O} \). However, the similarity of the data shown in the present paper for \( \mathbf{H} \) within the \( ab \)-plane implies that no significant difference exists between the behaviors of the Knight shifts of \( \mathrm{P}_2\text{-} \) and \( \mathrm{P}_3\text{-} \) superconductors. Then, we think that the singlet pairing is also realized in the present \( \mathrm{P}_3\text{-}\mathrm{Na}_{2}\text{CoO}_2\text{H}_2\text{O} \).

In Fig. 8, the longitudinal relaxation rate, \( 1/T_1 \) is plotted against \( T \) for \( ^{59}\text{Co} \) nuclei. In the figure, the data reported for \( \mathrm{P}_2\text{-}\mathrm{Na}_{2}\text{CoO}_2\text{H}_2\text{O} \)\(^{24,25}\) are also shown. We find that both the \( \mathrm{P}_2\text{-} \) and \( \mathrm{P}_3\text{-} \) \( \mathrm{Na}_{2}\text{CoO}_2\text{H}_2\text{O} \) systems exhibit similar \( T \) dependences of \( 1/T_1 \) and that they do not exhibit the coherence peak, confirming that their superconducting phases exhibit very similar behaviors. As has been already discussed in the preceding paper,\(^7\) it seems to be important, for the complete understanding of the superconducting state of the hydrated Co oxides, to have a consistent explanation of the behaviors of \( K \), \( 1/T_1 \) and the rather small effect of non-magnetic impurities on the superconducting transition temperature \( T_c \).\(^8\) It remains as a future problem.

Neutron scattering studies carried out for \( \mathrm{P}_2\text{-}\mathrm{Na}_{2}\text{CoO}_2\text{H}_2\text{O} \)\(^{24,25}\) and \( \mathrm{P}_2\text{-}\mathrm{Na}_{2}\text{CoO}_2\text{H}_2\text{O} \)\(^{24,25}\) have shown that the interlayer magnetic interaction of the electron system is so significant that the system has the 3-dimensional nature. It is also reported that the in-plane magnetic correlation is ferromagnetic for these Na-rich systems. It has been pointed out that the origin of this significant interlayer coupling takes place through the \( sp^2 \) hybridized orbits of \( Na^+ \) and \( O^{2-} \) ions between the \( \text{Co}_2 \) planes.\(^{26}\) Then, the neutron results stated above might indicate that the stacking way of the \( \text{Co}_2 \) layers, which affects the interlayer coupling, is important for the determination of the physical properties of \( \mathrm{Na}_{2}\text{CoO}_2\text{H}_2\text{O} \). However, various kinds of results obtained by NMR/NQR, neutron scattering and other studies on \( \mathrm{P}_2\text{-}\mathrm{Na}_{2}\text{CoO}_2\text{H}_2\text{O} \) indicate that the system has the low dimensional nature and the antiferromagnetic in-plane correlation of the electrons in the region of \( x \approx 0.6 \), as reported elsewhere.\(^{27}\) Moreover, it is expected for the superconducting systems with \( x \approx 0.3 \), the 2-dimensional nature is enhanced by the \( \text{H}_2\text{O} \) intercalation. Therefore, we think that the stacking way of the \( \text{Co}_2 \) planes does not have effects on the physical properties. It is consistent with the present experimental results.

4. Summary

We have presented the results of the \( ^{59}\text{Co} \)-NMR experiments for a randomly oriented sample of \( \mathrm{P}_3\text{-}\mathrm{Na}_{2}\text{CoO}_2\text{H}_2\text{O} \). The magnitude of the Knight shift \( K \) decreases with decreasing \( T \) below \( T_c \) for the field direction \( \mathbf{H} \) within the \( ab \)-plane. For this
reduction, the suppression of $\Delta K_{\text{spin}}$ is essential. The value of $H_{c2}(T=0)$ estimated from the $\Delta K(\text{H})-T$ curves is similar to those of P2-Na$_x$CoO$_2$yH$_2$O. The structural difference between P3- and P2-Na$_x$CoO$_2$yH$_2$O seems not to induce any significant differences between the superconducting properties of these two systems. In the strict sense, the present results do not completely exclude the possibility of the triplet pairing state with their spins strongly pinned along the $c$-axis. However, considering that $\Delta K_{\text{spin}}$ of P2-Na$_x$CoO$_2$yH$_2$O decreases with decreasing $T$ below $T_c$ even in the case of $H$ parallel to the $c$ direction, it is natural to conclude that the possibility of the triplet pairing is ruled out for the present P3-Na$_x$CoO$_2$yH$_2$O, too.

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