The discovery of superconductivity of bilayer water intercalated sodium cobalt oxides $\text{Na}_x\text{CoO}_2\cdot y\text{H}_2\text{O}$ (BLH) has renewed our interests in itinerant triangular lattice systems.\(^1\) After much experimental efforts have been devoted to find the chemical parameters on the superconducting transition temperature $T_c$, the complicated and delicate structural parameters on the Na vacancies, the intercalated water molecules and oxonium ions, which partially occupy the sodium site,\(^2\) have been revealed. However, the microscopic roles of these parameters in characterizing the superconductors are still poorly understood.

Recently we successfully synthesized powder samples of $\text{Na}_x\text{CoO}_2\cdot y\text{H}_2\text{O}$ with different superconducting transition temperature $T_c$ by a soft chemical method by utilizing so-called duration effect.\(^3\) The $T_c$ of a series of samples shows a systematic change with the increase of time duration after synthesis of bilayer $\text{Na}_x\text{CoO}_2\cdot y\text{H}_2\text{O}$ being kept in a humidified chamber (75 % relative humidity atmosphere). The another conditions of humidification atmosphere were independently found to lead to different duration effects, where $T_c$ also shows a systematic change.\(^4\) In contrast to the X-ray and neutron diffraction techniques, the $\text{Co}^{59}$ nuclear quadrupole resonance (NQR) is a powerful technique to investigate local electronic state around cobalt atoms. Thus we have performed $\text{Co}^{59}$ nuclear quadrupole resonance (NQR) studies on bilayer $\text{Na}_x\text{CoO}_2\cdot y\text{H}_2\text{O}$ prepared by using the duration effect to characterize the electronic states of CoO₂ planes and the electron spin dynamics microscopically.

The powder samples of bilayer water intercalated sodium cobalt oxides were prepared by the same way as mentioned in ref. 3. A monolayer water intercalated sodium cobalt oxide (MLH) was synthesized by a deintercalation method of water molecules from BLH in a dry N₂ gas flowing atmosphere.

The $\text{Co}^{59}$ (nuclear spin $I=7/2$) NQR experiments have been done for the powder samples by utilizing a coherent-type pulsed NMR spectrometer. The $\text{Co}^{59}$ nuclear spin-lattice relaxation time $T_{1\text{N}}$ was measured by an inversion recovery technique. The spin-echo signal $M(t)$ was measured as a function of long delay time $t$ after an inversion pulse, and $M(\infty)\equiv M(t > 10T_1)$ was recorded. All the recovery curves were measured at the peak frequency of $\nu_3$, which corresponds to the transition $I_z = \pm 5/2$ $\leftrightarrow$ $\pm 7/2$. In order to estimate $T_{1\text{N}}$, the recovery curves $p(t) = 1 - M(t)/M(\infty)$ were fitted by a theoretical $p(t) = p(0)[(3/7)e^{-3\gamma/7t} + (100/77)e^{-10t/T_1} + (3/11)e^{-21t/T_1}]$ for the transition ($I_z = \pm 5/2$ $\leftrightarrow$ $\pm 7/2$), where $p(0)$ and $T_1$ are fit parameters.\(^5\) Agreement of the theoretical and experimental recovery curves was totally satisfactory except for magnetically ordered states and also except for the samples near the boundary between the superconducting and magnetic phases in Fig. 2. The temperature dependence of the transverse relaxation curves was also measured using a spin echo technique for non-superconducting BLH. A production of Lorentzian ($T_{2\text{L}}$) and Gaussian ($T_{2\text{G}}$) terms with double time constants, $m(2\tau) = m(0)e^{-(2\tau/T_{2\text{L}}) - 1/2(2\tau/T_{2\text{G}})^2}$, was fitted to the data.

Figure 1 (a) shows the NQR spectra at 10 K on superconducting ($T_c = 2, 3.1, 3.7, 4.4$, and $4.6$ K) and non-superconducting BLH as well as MLH Na$_{3.7}$CoO$_2$·$\text{H}_2\text{O}$. These resonance lines arise from the transition, $I_z = \pm 5/2$ $\leftrightarrow$ $\pm 7/2$. In the superconductors BLH, the peak frequency of $\nu_3$ decreases as temperature increases as shown in Fig. 1 (b).

The MLH compound has an alternating stacking structure of Na/H$_2$O and CoO$_2$ layers. Four peaks in the NQR spectrum corresponding to $\nu_3$ suggest that at least four cobalt sites exist in the MLH. But we cannot assign these sites because of lack of information on the Na/H$_2$O...
local structure. The sodium ions and water molecules occupy just upper sites of oxygen sites along the c-axis in the MLH.\(^2\) The more than four cobalt sites with different NQR frequency \(\nu_3\) may be related with Na vacancy superlattice and oxonium ordering.

In the case of BLH, only a broad single peak of \(\nu_3\) appears in the NQR spectrum. The intercalated water molecules smear out the local electric field gradient around several cobalt sites. The BLH compounds, whose NQR spectra are shown in Fig. 1, were synthesized by a single set of time duration treatment mentioned in ref. 3. As the time duration in the humidified chamber and \(T_c\) increase, the peak frequency \(\nu_3\) of the NQR spectrum decreases without the change of line shape. If the oxygen content changes with the time duration, the NQR spectrum would be expected to show asymmetrically broadening as in the case of high-\(T_c\) cupper oxides. Thus the oxygen content in BLH is thought to be stoichiometric. From the analysis of X-ray powder diffractions,\(^3\) the lattice constants were nearly the same for the present samples. The cobalt valance in the BLH system is reported to be +3.4 and does not change so much.\(^3\) Thus, not the doped carriers but the local crystal shrink of CoO\(_6\) octahedrons changes with the time duration accompanied by the decrease of \(\nu_3\). The distortion of CoO\(_6\) octahedron may cause some change in the electronic state of CoO\(_2\) planes and then increase \(T_c\). Therefore, the value of \(\nu_3\) can be a measure of the change in the electronic state.

Figure 2 is a magnetic phase diagram of \(T_c\) plotted against \(\nu_3\) at 10 K, which was drawn from the results by the magnetic susceptibility and \(\nu_3\) from the \(^{59}\text{Co}\) NQR spectra measurements. \(T_M\) was determined by measurements of the nuclear spin relaxation rates as shown later. The closed circles in Fig. 2 were obtained for the present BLH samples in Fig. 1 (a). The open circles were obtained for the other BLH samples with the different duration effect using different initial mother compounds. The crosses in Fig. 2 denote the previous data on the accidentally obtained samples with various \(T_c\)’s.\(^7\) Because we study the samples with systematically changing \(T_c\) in this work, the consistency with the previous work suggests that the samples in ref. 7 are involved in the series of our samples. We found that \(T_c\) is suppressed near the boundary between the superconducting and the magnetic phases. The optimal \(T_c\) and the highest superconducting volume fraction are realized in the sample with \(\nu_3\sim12.30\) at 10 K.

The domed superconducting phase is similar to those of the high \(T_c\) cuprates. The similar dome shape phase diagram of \(T_c\) as a function of the sodium content in \(\text{Na}_x\text{CoO}_2y\text{H}_2\text{O}\) system is reported in ref. 8. However, the formal cobalt valence does not change with the different \((\nu_3, T_c)\) samples of the same sodium content. If the sodium content can be changed from a sample to another, the additional oxonium ions should compensate for the loss of charge to make cobalt valence almost invariant.\(^6\) Therefore, we believe that the coordinate of \((\nu_3, T_c)\) specifies the degree of the distortion of CoO\(_6\) octahedron, which may change the band structure.

We obtained several non-superconducting BLH samples by using the different initial and humidity conditions in the synthesis process. Figure 3 (a) shows the \(^{59}\text{Co}\) NQR spectra in one of the non-superconducting BLH samples at 2 and 10 K. The separable peaks at about 8.15 and 12.50 MHz correspond to the transition lines \(\nu_2\) \((I_z = \pm3/2 \leftrightarrow \pm5/2)\) and \(\nu_3\) \((I_z = \pm5/2 \leftrightarrow \pm7/2)\), respectively. At 10 K, the line shape and width are similar to those of the superconducting BLH samples except for a slight difference in the peak position of the resonance line. The line shapes of the superconducting BLH samples do not change so much in the superconducting state at 2 K. However, the line shape of the non-superconducting sample drastically changes at 2 K; the \(\nu_2\) line broadens both toward the lower and upper frequency sides while the \(\nu_3\) line shows broadening only to the lower frequency side. If these changes in the NQR
spectra arise from changes in electric field gradients with cooling, the change in the \( \nu_3 \) line should be scaled by that in the \( \nu_2 \) line. But the actual change was larger in \( \nu_2 \) than that in \( \nu_3 \). Therefore, the asymmetric broadenings in the \( \nu_2 \) and \( \nu_3 \) lines indicate the occurrence of an internal magnetic field. In general, the NQR spectrum of \( I = 7/2 \) would show broadening at the upper frequency side of \( \nu_3 \) under the small internal magnetic field parallel to the principal axis of the electric field gradient tensor (c-axis),\(^9\) suggesting that the small internal magnetic field should point in the \( \text{Co}_2\text{O}_2 \) plane in the present case. The broad but not split \( \nu_2 \) line suggests that the internal magnetic field distributes in the plane. The presence of such a small internal magnetic field in non-superconducting BLH is similar to that previously reported.\(^7\)

Figure 3 (b) shows the temperature dependence of the relaxation rates \( 1/T_{2L} \) and \( 1/T_{2G} \) in the non-superconducting BLH sample. The primary contribution to \( 1/T_{2L} \) is a \( T_1 \) process. \( 1/T_{2G} \) is a nuclear spin-spin relaxation rate. \( 1/T_{2G} \) increases with cooling below 50 K, indicating that an indirect nuclear spin-spin coupling enhances and the coupling constant with the static spin susceptibility increases below 50 K. At high temperatures above 100 K, the narrowing effect such as sodium motion may increase \( 1/T_{2L} \) and decrease \( 1/T_{2G} \). At 4.2 K, both \( 1/T_{2L} \) and \( 1/T_{2G} \) show abrupt changes. Taking into account the existence of the static internal magnetic field, the abrupt change in \( 1/T_{2L,G} \) and an anomaly in \( 1/T_1 \) (shown later), a kind of static magnetic ordering occurs at \( T_{M} \sim 4.2 \) K. The distributed internal magnetic field and the absence of conventional critical slowing down effect on \( T_2 \) and \( T_1 \) indicate an unconventional magnetic ordering such as a quasi-long range ordering.

Figure 4 shows the temperature dependence of the nuclear spin-lattice relaxation rate \( 1/T_1 \) in the non-superconducting and superconducting \( (T_c = 4.6 \text{ K}) \) BLH samples. In both cases, \( 1/T_1 \) shows a rapid decrease below \( T_c = 4.6 \text{ K} \) and \( T_M \sim 4.2 \) K, indicating that the elementary excitation spectrum changes at \( T_c \) and \( T_M \). At low temperatures in the paramagnetic state, both relaxation rates \( 1/T_1 \) show non-Korringa power law behavior \( (\sim T^n, n < 1) \) and the index \( n \) is near or less than 0.7. In the superconducting sample below \( T_c \), the power law index \( n \) is about 3 without coherence peak, indicating the presence of the line nodes in the superconducting gap parameter. The \( T \)-linear behavior of \( 1/T_1 \) in the wide range of the low temperatures indicates that the residual density of states is larger than that of the optimal superconducting BLH samples previously investigated.\(^{10,11}\) The appreciable residual density of states is a characteristic of the line-node superconductivity.

In the non-superconducting BLH, \( 1/T_1 \) does not show the critical divergence at \( T_M \). The \( 1/T_1 \) behavior near \( T_M \) resembles the case of the charge-density-wave transition. But at least the static internal magnetic field exists below \( T_M \). Below \( T_M, 1/T_1 \) shows the power raw behavior with \( n \sim 1.5 \). The \( T \)-linear behavior is expected in both the itinerant ferromagnetic and itinerant Néel states in \( T \ll T_M \) according to the self-consistent renormalization theory.\(^{12}\) Thus, the low lying excitation spectrum of the magnetically ordered state in the non-superconducting BLH is thought to be unconventional.

Figures 5 (a) and (b) show the temperature dependence of \( 1/T_1 T \) in logarithmic and linear scales, respectively. In addition to the non-superconducting and superconducting \( (T_c = 4.6 \text{ K}) \) BLH samples, \( 1/T_1 T \) in the superconducting BLH with \( T_c = 3.1 \text{ K} \) is shown. The sample with \( T_c = 3.1 \text{ K} \) is located near the boundary be-
between superconducting and magnetic phases in the phase diagram in Fig. 2. At low temperatures above $T_c$ and $T_M$, $1/T_1T$ increases with decreasing temperature due to the enhancement of the magnetic fluctuations, and decreases at the superconducting and magnetic phase transitions. The enhancement of $1/T_1T$ increases as $\nu_3$ increases, suggesting the magnetic correlations develop with $\nu_3$. Although $T_c$ increases with the enhancement of $1/T_1T$ and the magnetic correlations in the left side of the optimal $\nu_3 \sim 12.30$ MHz in Fig. 2 as well as the non-superconducting but magnetic BLH. We observed a dome shape superconducting phase with the optimal $\nu_3 \sim 12.30$ MHz. In the non-superconducting BLH, the $^{59}$Co NQR spectrum shows a broadening below $T_M$ without the critical slowing down effect of $1/T_1$ and $1/T_2$, indicating an unconventional magnetic ordering. From the analysis of the temperature dependence of the relaxation rates, we concluded that the magnetic fluctuations are enhanced above $T_c$ and $T_M$ with the increase of $\nu_3$. We observed that $T_c$ is suppressed near the phase boundary $\nu_3 \sim 12.50$ MHz, which may arise from the additional effects to cause an unconventional magnetic ordering. We thank Dr. T. Waki and Dr. M. Kato for their experimental supports, and Dr. K. Ishida, Mr. Y. Ihara and Dr. Sakurai for fruitful discussion. This work is supported by Grants-in Aid for Scientific Research on Priority Area "Invention of anomalous quantum materials", from the Ministry of Education, Culture, Sports, Science and Technology of Japan (16076210).

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