Electronic correlations and superconductivity in transition-metal oxides have been a main focus in condensed matter physics since the discovery of high-transition-temperature ($T_c$) superconductivity in copper oxides. The hydrated cobalt-oxide superconductor Na$_x$CoO$_2$·1.3H$_2$O has intensified the research interest in the past few years. This compound bears similarities to the high-$T_c$ copper oxides in that it has a quasi-two-dimensional crystal structure and contains a transition-metal element that carries a spin of $\frac{3}{2}$. Indeed, nuclear quadrupole resonance (NQR) measurements on Na$_x$CoO$_2$·1.3H$_2$O have found $T^3$ variation below $T_c$ in the spin-lattice relaxation rate $1/T_1$, which is a strong indication of existence of line nodes in the superconducting gap function. Precise measurements of the Knight shift in a high quality single crystal reveal that the spin susceptibility decreases below $T_c$ along both $a$- and $c$-axis directions, which indicates that the Cooper pairs are in the spin-singlet state. Thus, the superconductivity in Na$_x$CoO$_2$·1.3H$_2$O appears to be of $d$-wave symmetry, as in the case of high-$T_c$ copper oxides. It has also been found that antiferromagnetic spin correlations are present in the superconducting cobaltates, though being much weaker than those in the cuprates. The correlations are anisotropic in the spin space, which is different from the cuprate case.

Then, a natural question is how to model the cobalt oxides. Many authors applied the so-called $t$-$J$ model that had been widely used to describe the cuprates. In these theories, one virtually starts from CoO$_2$ in which Co is in the Co$^{4+}$ state and there is one electron ($s=1/2$ in the lowest level ($d_{1z}$ orbital). Upon adding Na, one dopes electrons into the $d_{1z}$ orbital and creates a Co$^{3+}$ ($s=0$) state. In such a scenario, one may be in a situation of dealing with a doped Mott insulator, as in the cuprates case. Therefore, it is important to synthesize the CoO$_2$ phase and to reveal its electronic ground state. Unfortunately, it has been chemically difficult to obtain pure phase of CoO$_2$, or even Na$_x$CoO$_2$ with $x\leq0.25$, though some efforts have been reported.

In this Rapid Communication, we report $^{59}$Co-NMR and NQR studies to uncover the electronic state and spin correlations in Li-deficient phases, Li$_x$CoO$_2$ ($x=0.35$, 0.25, and 0.12), and the CoO$_2$ phase. Although the antiferromagnetic spin correlation increases with reducing Li content ($x$), the end member, CoO$_2$, is a noncorrelated metal that well satisfies the Korringa relation for a Fermi liquid. Thus, CoO$_2$ is not simply located at the limit of the three dimensionality of the compound which is in contrast to the highly two-dimensional structure of A$_x$CoO$_2$.

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Spectroscopy determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) were in excellent agreement with the theoretical ones, indicating that the full amount of electricity due to the current was used for Li deintercalation from LiCoO$_2$. Since high-valent cobalt oxides tend to experience chemical instability when exposed to atmospheric moisture, sample handling and characterization were carefully made in an inert gas atmosphere. A part of the electrochemically treated samples (~70 mg) was encapsulated into a Pyrex ampule filled with Ar gas. NMR/NQR measurements were performed by using a phase-coherent spectrometer. The NQR measurements were performed at zero magnetic field. The NMR and NQR spectra were taken by changing the external magnetic field (H) at a fixed rf frequency of 71.1 MHz and by changing rf frequency and recording the spin-echo intensity step by step, respectively. The value of 1/T$_1$ was extracted by fitting the nuclear magnetization obtained by recording the spin-echo intensity to the master equation.$^{16,17}$

Figure 2(a) shows a representative $^{59}$Co-NMR spectrum for CoO$_2$. The spectrum shows a typical randomly oriented powder pattern. Since $^{59}$Co nucleus has nuclear spin I=7/2, an NMR spectrum has seven peaks due to the quadrupole interaction.$^{18}$ As schematically shown by solid and dotted arrows in Fig. 2(a), the observed spectrum consists of two central peaks that originated from the anisotropy of the Knight shift along the ab-($K_{ab}$) and c-($K_c$) directions and each central peak is accompanied by six satellite peaks. The numerical calculation considering the quadrupole effect up to the second-order perturbation completely reproduced the experimental result [solid curve in Fig. 2(a)]. The clear peak structure attests the high quality of the sample. Thus, we are able to obtain the values of $K_{ab}$ and $K_c$ precisely from the NMR spectra. Figure 2(b) shows the $^{59}$Co-NQR spectra for Li$_x$CoO$_2$ ($x$=0.0, 0.12, and 0.35) observed at zero magnetic field. As in Na$_x$CoO$_2$·yH$_2$O, three NQR transition lines arising from I=7/2 are clearly observed in Li$_x$CoO$_2$. For $x$=0.35, satellite peaks are observed as indicated by the arrows in Fig. 2(b). It indicates that a secondary phase is present in this composition, although x-ray diffraction immediately after sample synthesis showed a single-phase pattern. Since these peaks increased in intensity as time elapsed (not shown), this is an extrinsic phase that arises after the x-ray diffraction analysis.

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**FIG. 1.** (Color online) X-ray powder diffraction patterns for (a) CoO$_2$, (b) Li$_{1/3}$CoO$_2$, (c) Li$_{1/3}$CoO$_2$, and (d) Li$_{0.33}$CoO$_2$ samples. For these samples, Rietveld refinement of the crystal structure was unsuccessful as the use of an airtight sample holder had significantly deteriorated the resolution of the diffraction patterns.

Sharp diffraction peaks throughout the XRD patterns demonstrate that our Li$_x$CoO$_2$ and CoO$_2$ samples are chemically homogenous with good crystallinity. The actual x values determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) were in excellent agreement with the theoretical ones, indicating that the full amount of electricity due to the current was used for Li deintercalation from LiCoO$_2$. Since high-valent cobalt oxides tend to experience chemical instability when exposed to atmospheric moisture,

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**FIG. 2.** (Color online) (a) $^{59}$Co NMR spectrum for CoO$_2$ measured at T=4.2 K. The NMR frequency is 71.1 MHz. Solid and dotted arrows indicate the two sets of seven NMR peaks originated from anisotropy of the Knight shift, respectively. (b) NQR spectra for Li$_x$CoO$_2$ ($x$=0.0, 0.12, and 0.35) measured at T=4.2 K. Arrows indicate that extrinsic NQR peaks occurred due to aging (degradation). (c) and (d) are typical data sets of $^{59}$Co nuclear recovery curves for CoO$_2$ obtained by NMR and NQR, respectively (see text).
TABLE I. NQR parameters for Li$_x$CoO$_2$ obtained at 4.2 K.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{59}v_Q$ (MHz)</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoO</td>
<td>2.93</td>
<td>0.05 ± 0.01</td>
</tr>
<tr>
<td>Li$_{0.12}$CoO$_2$</td>
<td>3.76</td>
<td>0.09 ± 0.01</td>
</tr>
<tr>
<td>Li$_{0.35}$CoO$_2$</td>
<td>4.32</td>
<td>0.10 ± 0.02</td>
</tr>
</tbody>
</table>

Figures 2(c) and 2(d) show typical data sets of $^{59}$Co nuclear recovery curves to obtain $T_1$ by NMR and NQR, respectively. As drawn in solid curves in figures, they can be fitted by single component of theoretical curves even though the $T_1$ is measured in powdered sample. Compared to the early report in which the NMR spectrum did not show clear peak structure since it was a superposition of signals from different phases and $T_1$ is not of single component, it is obvious that the present sample has much better quality, and the result represents, we believe, the intrinsic property of CoO$_2$.

The NQR parameters are summarized in Table I. Here $v_0$ and asymmetry parameter $\eta$ are defined as $v_0 = v_c = \frac{1}{2}\sqrt{\frac{3Q_{x-y}^2 + 2}{2}}$, with $Q$ and $\frac{2V}{Q_{x-y}}(\alpha=x,y,z)$ being the nuclear quadrupole moment and the electric field gradient (EFG) at the position of the Co nucleus, respectively. Notably, $v_0$ increases with increasing $x$. This assures electron doping by the increase in Li content. On the other hand, $\eta$ is almost the same in $x=0.12$ and 0.35 but is substantially reduced in CoO$_2$. This is because the CoO$_2$ phase crystallizes in a simple structure containing CoO$_2$ layers only (the so-called O1-type structure), while the crystal of Li$_x$CoO$_2$ consists of alternate stacking of Li$_x$ and CoO$_2$ blocks.

Figure 3(a) shows the $T$ dependence of the Knight shift ($K_{ab}$ and $K_c$) for three samples with different Li contents. As clearly seen in the figure, both $K_{ab}$ and $K_c$ of Li$_x$CoO$_2$ do not depend on temperature. Here, the Knight shift consists of contributions from the spin susceptibility, $K_s$, and from the orbital susceptibility (Van Vleck susceptibility), $K_{orb}$, of Li$_x$CoO$_2$, and from the orbital susceptibility (Van Vleck susceptibility), $K_{orb}$, of Li$_x$CoO$_2$ (Ref. 11). Figure 3(b) shows the $T$ dependence of $1/T_1T$ measured by $^{59}$Co NMR with $H//ab$. Surprisingly, the $1/T_1T$ for CoO$_2$ is $T$ independent. Together with the $T$-independent Knight shift in CoO$_2$, the Korringa relation is satisfied as will be discussed later in more detail. This is a strong and the first evidence for a weakly correlated ground state of CoO$_2$.

De Vaulx et al. suggested that CoO$_2$ is a strongly correlated system on the basis of a small value of the characteristic temperature, $T^*$, below which the Korringa relation holds. However, as seen in Fig. 3(b) inset, we find that their result is similar to the result for our Li$_{0.12}$CoO$_2$ sample. As the authors acknowledged, their sample contained a Li-rich phase as impurity. We suggest that the present results clarify the true electronic state of CoO$_2$.
Li$_x$CoO$_2$ crystallizes in a less anisotropic structure. Since there is no "spacer" layer between two adjacent CoO$_2$ blocks when $x=0$ end member of the families $A_x$CoO$_2$ ($A=Li,Na$) with small $x$ is viewed as a doped spin 1/2 system. Due to the abrupt change in the electronic state is clearly due to the abrupt change in the crystal structure. The $Li_x$CoO$_2$ phase with finite $x$ has a highly two-dimensional crystal structure in which the interlayer Co-Co distance ($d_{Co-Co}$) is as large as 5.0–5.1 Å, while CoO$_2$ crystallizes in a less anisotropic structure. Since there is no “spacer” layer between two adjacent CoO$_2$ blocks when Li ions are completely extracted, the $d_{Co-Co}$ value is reduced to 4.24 Å in CoO$_2$. The emergent three dimensionality is believed to be the origin of the weak electron correlation of CoO$_2$.

Finally, we examine if there exists any renormalization effect in CoO$_2$. To this end, we evaluate the Korringer ratio, $S = T_1^\text{HS} = \frac{4\pi^2}{h} \frac{\langle \mu \rangle^2}{N_e}$ This quantity is unity for a free-electron system. It is much smaller than the unity for an antiferromagnetically correlated metal but much larger than the unity for a ferromagnetically correlated metal. In the present case, we use the $K_{\text{HS}}^\text{Co}=2.96%$ and $K_{\text{HS}}^\text{Co}=1.72%$ obtained from recent NMR study in single-crystalline Na$_{0.42}$CoO$_2$ and then we obtain $S=1.12 \pm 0.04$ for CoO$_2$. Therefore, CoO$_2$ is a conventional metal that well conforms to Fermi-liquid theory.

In conclusion, we have presented $^{59}$Co-NMR and NQR measurements and analysis on $Li_x$CoO$_2$ ($x=0.0–0.35$). The antiferromagnetic-like spin fluctuations develop when Li is deintercalated from Li$_{0.35}$CoO$_2$, which is consistent with the picture that the member of the families $A_x$CoO$_2$ ($A=Li,Na$) with small $x$ is viewed as a doped spin 1/2 system. Due to the emergent three dimensionality of the crystal structure, however, CoO$_2$, the $x=0$ end member of $A_x$CoO$_2$, is a conventional metal that well conforms to Fermi-liquid theory. The result highlights the importance of two dimensionality for electron correlations in $A_x$CoO$_2$, as was the case that water intercalated into noncorrelated Na$_{0.42}$CoO$_2$ brings about spin fluctuations. We hope that these results form a foundation for understanding cobalt oxides and the superconductivity developed out of there.

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