CoO$_2$ is the parent compound for the superconductor Na$_x$CoO$_2\cdot$1.3H$_2$O and was widely believed to be a Mott insulator. We performed $^{59}$Co nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) studies on Li$_x$CoO$_2$ ($x=0.35, 0.25, 0.12$, and $0.0$) to uncover the electronic state and spin correlations in this series of compounds which was recently obtained through electrochemical de-intercalation of Li from pristine LiCoO$_2$. We find that although the antiferromagnetic spin correlations systematically increase with decreasing Li-content ($x$), the end member CoO$_2$ is a non-correlated metal that well satisfies the Korringa relation for a Fermi liquid. Thus, CoO$_2$ is not simply located at the limit of $x \rightarrow 0$ for A$_x$CoO$_2$ ($A=\text{Li, Na}$) compounds. The disappearance of the electron correlations in CoO$_2$ is due to the three dimensionality of the compound which is in contrast to the highly two dimensional structure of A$_x$CoO$_2$.

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\cdot$1.3H$_2$O has intensified the research interest in the past few years[1]. This compound bears similarities to the high-$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 $\frac{1}{2}$. Indeed, nuclear quadrupole resonance (NQR) measurements on Na$_x$CoO$_2\cdot$1.3H$_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 [2, 3, 4]. Precise measurements of the Knight shift in a high quality single crystal reveals 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 [5]. Thus, the superconductivity in Na$_x$CoO$_2\cdot$1.3H$_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 [2, 3]. The correlations are anisotropic in the spin space [6], 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 [2, 8, 9]. 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 ($a_{1g}$ orbital). Upon adding Na, one dopes electrons into the $a_{1g}$ 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 [7, 8, 10]. Therefore, it is important to synthesize the CoO$_2$ phase and 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 $x < 0.25$, though some efforts have been reported [11, 12, 13].

In this paper, 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 found to be a non-correlated metal that well satisfies the Korringa relation for a Fermi liquid. The result obtained from our CoO$_2$ sample is different from the one reported earlier [11] in both the temperature ($T$) dependence and the magnitude of the $1/T_1$. It turns out that the earlier result correspond to that of our Li$_{0.12}$CoO$_2$. We argue that, however, the disappearance of the electron correlations in pure CoO$_2$ is due to the three dimensionality of the compound which collapses from the highly two dimensional structure of A$_x$CoO$_2$ ($A=\text{Li, Na}$) when Li is completely removed. The systematic evolutions of the electron correlations in Li$_x$CoO$_2$ ($x=0.35, 0.25$, and $0.12$), as well as in Na$_x$CoO$_2\cdot$1.3H$_2$O ($x=0.35, 0.33, 0.28$, and $0.25$) [3], are consistent with the theoretical postulation that A$_x$CoO$_2$ ($A=\text{Li, Na}$) with small $x$ be near a magnetic instability [7, 8].
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\[16, 17\].

Polycrystalline samples of \( \text{Li}_x\text{CoO}_2 \) \((x = 0.35, 0.25, \) and \( 0.12)\) and \( \text{CoO}_2 \) \((x = 0.0)\) were synthesized through electrochemical de-intercalation of Li from pristine \( \text{LiCO}_2\) as described elsewhere \[14, 15\]. Approximately 100 mg of single-phase \( \text{LiCO}_2\) pellet (without additives) was electrochemically oxidized with a constant current of 0.1 mA in an airtight flat cell filled with a nonaqueous electrolyte. The Li content \((or the amount of Li ions to be extracted)\), i.e. \(1-x)\) of each sample was precisely controlled by the reaction duration based on Faraday’s law. Typically, a 100-mg \( \text{LiCO}_2\) pellet was charged for 178, 205, 241, and 274 h to obtain the \( x = 0.35, 0.25, 0.12, \) and 0.0 \((i.e. \text{CoO}_2)\) phases, respectively. As seen in Fig.1, x-ray powder diffraction analysis evidenced that all the samples are of single phase with characteristic crystal structures typical for their Li compositions. Sharp diffraction peaks throughout the XRD patterns demonstrate that our \( \text{Li}_x\text{CoO}_2\) and \( \text{CoO}_2\) 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 de-intercalation from \( \text{LiCO}_2\). 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 \((\sim70 \text{ mg})\) was encapsulated into a Pyrex ampule filled with Ar gas. NMR/NQR measurements

![FIG. 1: (Color online) X-ray powder diffraction patterns for (a) \( \text{CoO}_2\), (b) \( \text{Li}_{0.12}\text{CoO}_2\), (c) \( \text{Li}_{0.25}\text{CoO}_2\), and (d) \( \text{Li}_{0.35}\text{CoO}_2\) 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.](image1)

![FIG. 2: (Color online) \((a)\) \(^{59}\text{Co}\) NMR spectra for \( \text{CoO}_2\) measured at \( T = 4.2 \text{ K} \). 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 spectrum for \( \text{Li}_x\text{CoO}_2 \) \((x = 0.0, 0.12, \) and 0.35) measured at \( T = 4.2 \text{ K} \). Arrows indicate extrinsic NQR peaks occurred due to aging (degradation). \((c)\) and \((d)\) are typical data sets of \(^{59}\text{Co}\) nuclear recovery curves for \( \text{CoO}_2\) obtained by NMR and NQR, respectively (see text).](image2)
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 increase in intensity as time elapsed (not shown), this is an extrinsic phase that arises after the X-ray diffraction analysis.

Figures 2 (c) and (d) show typical datasets 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 [16, 17], 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 [11], 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 1. Here $\nu_Q$ and asymmetry parameter $\eta$ are defined as $\nu_Q = \nu_x \equiv \nu_z = \frac{3}{2(2l+1)}g_\alpha^2Q \frac{\partial^2V}{\partial \alpha^2}$, with $Q$ and $\frac{\partial^2V}{\partial \alpha^2}$ ($\alpha = x, y, z$) being the nuclear quadrupole moment and the electric field gradient (EFG) at the position of the Co nucleus, respectively. [13] Notably, $\nu_Q$ increases with increasing $x$. This assures electron doping by the increasing of 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 OI-type structure), while the crystal of Li$_2$CoO$_2$ consists of alternate stacking of Li$_x$ and CoO$_2$ blocks. [14].

TABLE I: NQR parameters for Li$_x$CoO$_2$ obtained at 4.2 K.

| sample          | $^{59}\nu_Q$ (MHz) | $\eta$    |
|-----------------|---------------------|-----------|
| CoO$_2$         | 2.93                | 0.05±0.01 |
| Li$_{0.12}$CoO$_2$ | 3.76                | 0.09±0.01 |
| Li$_{0.35}$CoO$_2$ | 4.32                | 0.10±0.02 |

Figures 3 (a) shows the $T$ dependence of the Knight shift ($K_{ab}$ and $K_c$) for three samples with different Li content. 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), $K_{orb}$. $K_s = K_s + K_{orb}$, with $K_{orb}$ being $T$-independent but $K_s$ being $T$-dependent generally. $K_s(T)$ and $K_{orb}$ are respectively related to the spin susceptibility $\chi_s$ and orbital susceptibility $\chi_{orb}$ as $K_s(T) = A_{hf}\chi_s(T)$ and $K_{orb} = A_{orb}\chi_{orb}$, where $A_{hf}$ is the hyperfine coupling constant between the nuclear and the electron spins. The results show that the spin susceptibility in Li$_2$CoO$_2$ is $T$-independent.

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 discussed later in more detail. This is a strong and the first evidence for a weakly-correlated ground state of CoO$_2$.

De Vaux et al [11] 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 almost the same as that for our Li$_{0.12}$CoO$_2$ sample. As the authors acknowledged [11], their sample contained a Li-rich phase as impurity. We suggest that the present results clarify, for the first time, the true electronic state of CoO$_2$.

We further measured the $T_1$ systematically by $^{59}$Co-NQR at zero magnetic field, which corresponds to the configuration of $H//c$-axis since the principal axis of the EFG is along the $c$-axis. As shown in Fig 4, the $T$ dependence of $1/T_1T$ shows systematic change with decreasing Li-content, except for CoO$_2$ which will be discussed separately later. With decreasing $x$ from 0.35 to 0.12, $1/T_1T$ increases with decreasing $T$, indicating...
that the electron correlations are induced. Also, the increasing is more pronounced in samples with smaller x, which indicates that the spin correlation is stronger in samples with smaller x. A similar situation was encountered in Na_xCoO_2·1.3H_2O (x = 0.35, 0.33, 0.28, and 0.25) [3]. As in that case, the correlation is antiferromagnetic in origin since the Knight shift is T-independent. The 1/T_1T becomes constant below T^*, indicating a renormalized Fermi liquid state below T^*. This situation resembles that in electron-doped cuprate Pr_0.91LaCe_0.09CuO_4 where T^* ~60 K [19]. Furthermore, T^* decreases from 50 K for x = 0.25 to 7 K for x = 0.12. This also indicates that a sample with smaller x is closer to a magnetic instability. Therefore, the results are consistent with the theories for a compound near a magnetic transition [7, 8].

However, 1/T_1T is constant for CoO_2. This abrupt change in the electronic state is clearly due to the abrupt change in the crystal structure. The Li_xCoO_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 Korringa ratio, S = T_1(T)/T_1 = K_{orb}^0 (2\pi k_B T)^2. This quantity is unity for a free electron system. It is much smaller than the unity for a antiferromagnetically correlated metal but much larger than the unity for a ferromagnetically correlated metal [20]. In the present case, we use the K_{orb}^0 = 2.96% and K_{orb} = 1.72% obtained from recent NMR study in single crystalline Na_{0.42}CoO_2 [6], then we obtain S = 1.12±0.04 for CoO_2. Therefore, CoO_2 is a conventional metal that well conforms to Fermi liquid theory.

In conclusion, we have presented ^59Co-NMR and NQR measurements and analysis on Li_xCoO_2 (x =0.0−0.35). The antiferromagnetic-like spin fluctuations develop when Li is de-intercalated from Li_{0.35}CoO_2, which is consistent with the picture that the member of the families A_xCoO_2 (A = Li, Na) with small x be 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_xCoO_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_xCoO_2, as was the case that water intercalated into non-correlated Na_{0.42}CoO_2 brings about spin fluctuations [6]. We hope that these results form a foundation for understanding cobalt oxides and the superconductivity developed out of there.

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