The recent discovery of superconductivity in hydrated Na$_2$CoO$_2$·$\frac{1}{3}$H$_2$O ($T_c \sim 4.5\text{K}$) has generated considerable excitement [1–7]. It appears that the symmetry of the superconducting energy gap is unconventional [5], and the first $\text{Na}_2\text{CoO}_2$ triangular lattice systems tend to slow down to form a “120 degree” non-collinear structure as sketched in Fig.1(a). The residual tendency toward charge differentiation, and whether or not p-d hybridization induces sizable spin polarization in the O triangular lattice layers. Water intercalation makes CoO$_2$ planes homogeneous, and enhances low frequency spin fluctuations near $T_c = 4.5\text{K}$ at some finite wave vectors different from both the ferromagnetic and “120 degree” modes.

76.60.-k, 75.10.Jm
conducting phase was obtained by soaking some portion of $^{17}$O enriched Na$_{0.35}$CoO$_2$ ceramics in purified water. We verified that for $^{59}$Co, the $\pm \frac{2}{3}$ to $\pm \frac{1}{3}$ NQR frequency $^{59}\nu_{NQR} = 12.3$MHz and $^{59}1/T_1 T_{NQR} = 18$ sec$^{-1}$K$^{-1}$ observed just above $T_c$ agree very well with earlier reports [5]. We also confirmed that $^{59}1/T_1 T$ measured in zero field by NQR dips below $T_c$ as shown in Fig.4(c). We note that these properties are sensitive to the occupancy of Na$^{+}$ sites nearby. In contrast with these $^{17}$O NMR lineshapes for three samples. Since $^{17}$O has a nuclear spin $I = \frac{1}{2}$, one would expect the aligned ceramics of Na$_{0.72}$CoO$_2$ and Na$_{0.35}$CoO$_2$ to show only five resonance peaks from $m_z = m_z + 1$ transitions, if all O sites within CoO$_2$ layers are electronically equivalent. However, the observed $^{17}$O NMR lines in Fig.2(a) and (b) are a superposition of two sets of signals with nearly axially symmetric Knight shift and quadrupole interaction tensors. Na$_{0.72}$CoO$_2$ has O(A) and O(B) sites, as marked in Fig.2(a) by two sets of arrows, with relative integrated intensity of $\sim 0.7$ and $\sim 0.3$. We recall that $^{59}$Co NMR also shows two inequivalent sites, Co(A) and Co(B) sites with relative intensity of $\sim 0.7$ and $\sim 0.3$ due to charge differentiation. Co(A) is the Co$^{+3}$-like site with $S \sim 0$, while Co(B) is Co$^{+4}$-like site with $S \sim \frac{1}{2}$. Our new $^{17}$O NMR data indicate that the differentiation of the local Co electronic environments propagates to the adjacent O layers through $p$-$d$ hybridization. Na$_{0.35}$CoO$_2$ also exhibits two types of O sites, O(C) and O(D), with roughly comparable intensities. Unlike Na$_{0.72}$CoO$_2$, however, the difference in the local electronic environment at O(C) and O(D) sites is mild. This is consistent with our earlier finding from Co NMR studies that the tendency toward charge differentiation is strongly suppressed in the Fermi liquid phase [7].

We also found that the thermal motion of Na$^{+}$ ions above 220K results in motional narrowing, and O(C) and O(D) lines gradually merge into a single line (notice that the Knight shift $^{17}K(C) \sim ^{17}K(D)$ at 295 K in Fig.3). This suggests that O(C) and O(D) sites are differentiated by the occupancy of Na$^{+}$ sites nearby. In contrast with these unhydrated samples, Fig.2(c) shows that the lineshape of the unaligned superconducting sample Na$_3$CoO$_2 \cdot \frac{4}{3}$H$_2$O is a typical powder pattern from a single O site, with a nearly isotropic NMR Knight shift $^{17}K (\sim 0.11\%$ at 140 K) and a nearly axially symmetric nuclear quadrupole interaction tensor. This immediately leads us to conclude that water intercalation completely suppresses the residual tendency toward charge differentiation in O layers in the Fermi liquid phase Na$_3$CoO$_2$. The detailed structural analysis showed that four water molecules surround each Na$^+$ ions [10], and our results suggest that the Coulomb potential from the latter on CoO$_2$ planes is shielded by the former, thereby smoothing out the CoO$_2$ layers to make it superconducting.

It is convenient to employ $^{17}$O NMR Knight shifts $^{17}K = (^{17}f - ^{17}f_0)/^{17}f_0$ to make more quantitative comparison of charge differentiated O sites in Na$_x$CoO$_2$. $^{17}f$ is the observed $m_z = -\frac{2}{3} to +\frac{1}{3}$ central peak frequency, $^{17}f_0 = ^{17}\gamma_n B = 46.18$MHz is the bare resonance frequency if there were no magnetic hyperfine interactions between Co electron spins and O nuclear spins ($^{17}\gamma_n = 5.772$MHz/Tesla and $B = 8$ Tesla). Using the local spin susceptibility $\chi_{spin}$ at the j-th Co sites, the $^{17}$O Knight shift may be written as

$$^{17}K = ^{17}K_{spin} + ^{17}K_{orb} = \sum_j A_j \chi_{spin}^j + ^{17}K_{orb}, \quad (2)$$

where $^{17}K_{orb}$ represents the temperature independent orbital contribution (typically 0.1% or less [11]).

Fig. 3 summarizes the temperature dependence of $^{17}K$ at various O sites in three samples. Notice that $^{17}K \sim 0.1\%$ in all cases except at O(B) sites in Na$_{0.72}$CoO$_2$ (the vertical scale for the O(B) sites is separately shown on the right hand side of Fig. 3). The observed magnitude of $^{17}K$ is somewhat smaller than typical values observed for the in-plane O sites in high $T_c$ cuprates (0.1%−0.3% [12]), but quite sizable. In other words, p-$d$ hybridization introduces sizable electron spin polarization in Oxygen p orbitals of CoO$_2$ layers. Hence we cannot ignore the roles played by p orbitals in the electronic properties of these materials. Another important point to emphasize is that $^{17}K(B)$ at O(B) sites is extraordinarily large, and exceeds 1 %. Likewise, Co(B) sites exhibit a huge NMR Knight shift (up to $\sim 9\%$), while the Co(A) sites have nearly an order of magnitude smaller spin contribution [7]. Both $^{17}K(A)$ at O(A) sites and $^{17}K(B)$ show an identical Curie-Weiss temperature dependence as the bulk averaged magnetic susceptibility data and $^{59}$Co Knight shifts at Co(A) and Co(B) sites [7]. The solid curves are a Curie-Weiss fit with a constant background (presumably from the orbital effects $^{17}K_{orb}$), with a common Weiss temperature $\theta = -29\pm 3$ K. Our present $^{17}K$ data and the relative intensities of O(A) and O(B) sites strongly suggest that p orbitals at O(B) sites have strong hybridization with the d orbitals at Co(B) sites, but O(A) sites experience only mild effects from Co(B) sites. Notice that if each Co(B) site bonds equally with all six n.n. O sites, the intensity of O(B) sites would be factor 3 larger and account for $\sim 0.9$ of the total integrated intensity. Instead, our NMR results indicate that Co(B) sites transfer their spins primarily to one of the three n.n. O sites in each of the O layers above and below the Co layers. This somewhat unexpected result should be taken into account in the debate over the magnetic interlayer couplings and the local symmetry of Co and O orbitals. For example, recent neutron scattering measurements [13] showed that Co-Co inter-layer exchange interactions in Na$_{0.82}$CoO$_2$ are comparable to intra-layer
exchange interactions despite its layered structure. There is no doubt that the similar Co(B)-O(B)-Na-O(B)-Co(B) exchange path is responsible for the unexpectedly large inter-layer coupling.

Next, we discuss the local low frequency spin fluctuations as observed by the \( ^{17} \)O NMR spin-lattice relaxation rate \( T_1/T_1(T) \) (see Fig. 4). We found that the temperature dependence of \( T_1/T_1(T) \) in \( \text{Na}_0.72\text{CoO}_2 \) satisfies the same Curie-Weiss behavior as the local \( q = 0 \) susceptibility as measured by \( ^{17} \)K. This suggests that the ferromagnetic mode of Co spin fluctuations is enhanced within each CoO\(_2\) layer, and is consistent with the recent report of a type-A antiferromagnetic order with in-plane ferromagnetic correlations [14,13]. In contrast, \( T_1/T_1(T) \) shows qualitatively the same decrease with temperature as \( ^{17} \)K in \( \text{Na}_{0.35}\text{CoO}_2 \). The constant behavior of both \( T_1/T_1(T) \) and \( ^{17} \)K below \( \sim \)100K is consistent with a Korringa law \( T_1/T_1(T)^{{^{17} \kappa}} = \text{const.} \) and resistivity \( \rho \sim T^2 \) [3], both expected for a Fermi liquid [3].

Interestingly, \( ^{17,59} \)\( T_1/T_1(T) \) and \( ^{17} \)K in the hydrated superconducting sample \( \text{Na}_4\text{CoO}_4 \cdot \frac{4}{3}\text{H}_2\text{O} \) are similar to O(D) sites in the non-superconducting \( \text{Na}_{0.35}\text{CoO}_2 \) down to \( \sim \)50 K. However, \( ^{17} \)K remains constant near \( T_c \) while both \( ^{17} \text{CoO}_2 \) and \( ^{59} \text{CoO}_2 \) increase toward \( T_c = 4.5 \)K. The latter implies the enhancement of low frequency spin fluctuations before superconductivity sets in. Aside from the cleaner \( \text{CoO}_2 \) planes, this is the only major difference in the local electronic properties between the non-superconducting \( \text{Na}_4\text{CoO}_2 \) and superconducting \( \text{Na}_4\text{CoO}_2 \cdot \frac{4}{3}\text{H}_2\text{O} \). As such, it is natural to speculate that these enhanced spin fluctuations are responsible for, or at least related to, the mechanism of superconductivity. The question is, where in \( q \)-space are spin fluctuations enhanced? Given the ferromagnetic nature of in-plane spin correlations in \( \text{Na}_4\text{CoO}_2 \) with \( x = 0.72 \) or higher, one obvious possibility is near \( q = 0 \). However, \( ^{17} \)K in Fig.3 (as well as \( ^{59} \)K at \( ^{59} \)Co sites [7]) does not show enhancement near \( T_c \), hence we can rule out the ferromagnetic scenario. We note that magnetic defects and/or impurities easily contaminate the bulk susceptibility data of \( \text{Na}_4\text{CoO}_2 \cdot \frac{4}{3}\text{H}_2\text{O} \) to give a false Curie behavior near \( T_c \). The advantage of NMR Knight shifts is that defect spins only broaden the NMR lineshapes without affecting the temperature dependence.

Alternately, if the frustrated 120 degree mode of spin fluctuations have a large spin-spin correlation length, and grow toward \( T_c \) near the wave vector \( q = (\frac{1}{3}, \frac{1}{3}, 0) \), then \( ^{59} \text{CoO}_2 \) could grow without an increase of \( ^{17} \)K. However, such a scenario seems inconsistent with an identical increase observed for \( ^{17} \text{CoO}_2 \). Since the hyperfine form factor satisfies \( A(\frac{1}{3}, \frac{1}{3}, 0) = 0 \), \( ^{17} \text{CoO}_2 \) should show little enhancement toward \( T_c \). In other words, the frustrated “120 degree” configuration seems irrelevant in the low frequency properties of \( \text{Na}_4\text{CoO}_2 \cdot \frac{4}{3}\text{H}_2\text{O} \) near \( T_c \) [17].

To summarize the results for superconducting \( \text{Na}_4\text{CoO}_2 \cdot \frac{4}{3}\text{H}_2\text{O} \), spin fluctuations grow toward \( T_c \) at some finite wave vectors, which are different from the ferromagnetic \( q = 0 \) and frustrated \( q = (\frac{1}{3}, \frac{1}{3}, 0) \). This may be an indication that the carrier-doped triangular lattice favors a quantum spin liquid state. Given that recent ARPES measurements revealed a large Fermi surface in \( \text{Na}_4\text{CoO}_2 \) [15,16], the Fermi surface geometry may play a crucial role in deciding the nature of spin fluctuations, perhaps through nesting effects for a large \( |q| \) value(s). Putting all the pieces together, the strongly correlated electron behavior above \( T_c \) of \( \text{Na}_4\text{CoO}_2 \cdot \frac{4}{3}\text{H}_2\text{O} \) shares remarkable similarities with high \( T_c \) cuprates despite the triangular lattice geometry.

FIG. 1. (a) The \( \text{CoO}_2 \) layers of \( \text{Na}_x\text{CoO}_2 \). Arrows represent a classically stable, frustrated “120 degree” spin configuration. Notice that the hyperfine fields at \( ^{17} \)O sites cancel out in such a configuration. (b) The hyperfine form factor \( |A(q)|^2 \) at the O sites in \( \text{CoO}_2 \) layers plotted in the reciprocal space. The arrow marks the \( q = (\frac{1}{3}, \frac{1}{3}, 0) \) point where \( |A(q)|^2 = 0 \).
FIG. 2. (a) $^{17}$O NMR lineshape of Na$_{0.72}$CoO$_2$ observed with $B = 8$ Tesla applied along the magnetically aligned ab plane. We applied an inversion pulse and waited for 2 msec before recording the spin echo intensity to separate the O(B) sites with “Fast” relaxation times. By taking the difference between the whole echo intensity ("Slow") and the “Fast” O(B) contributions, we deduced the lineshape of O(A) sites (“Difference”). The vertical arrows identify five $m_z$ to $m_z + 1$ transitions of $^{17}$O (nuclear spin $I = \frac{5}{2}$). (b) $^{17}$O NMR lineshape of aligned Na$_{0.35}$CoO$_2$. (c) The powder pattern $^{17}$O NMR lineshape of Na$_4$CoO$_2$·$\frac{3}{4}$H$_2$O ceramics. The less pronounced peak structures and the high and low frequency tails are due to random orientations of the sample.

FIG. 3. $^{17}$K observed for various $^{17}$O sites identified in Fig.2. The solid lines are a best fit to a Curie-Weiss law with a constant offset, $^{17}K(A) = 4.2/(T + 29) + 0.024 \%$, and $^{17}K(B) = 38/(T + 29) + 0.11 \%$.

FIG. 4. $^{17}$O and $^{59}$Co $1/T_1T$ in (a) Na$_{0.72}$CoO$_2$, (b) Na$_{0.35}$CoO$_2$, and (c) Na$_4$CoO$_2$·$\frac{3}{4}$H$_2$O. In (a), red and blue solid curves represent a best fit to a Curie-Weiss behavior with the same negative Weiss temperature found for $^{17}$K in Fig.3, $^{17}1/T_1T = 29/(T + 29) + 0.2$ sec$^{-1}$K$^{-1}$ for O(A) and $^{17}1/T_1T = 88/(T + 29) + 0.08$ sec$^{-1}$K$^{-1}$ for O(B). The black curve is $^{59}1/T_1T = 241/(T + 29) + 5.8exp(-208/T)$ sec$^{-1}$K$^{-1}$, i.e. the same form of a Curie-Weiss term, plus an activation-type term with an energy gap 208 K. The $^{59}$Co NMR data in (a) and (b) are from Ning et al. [7].
\[ |A(q)|^2 \text{ [arb. units]} \]
(a) \( \text{Na}_{0.72} \)
140K

(b) \( \text{Na}_{0.35} \)
140K

(c) \( \text{Na}_{\frac{1}{3}} - \text{H}_2\text{O} \)
77K

\( F \) [MHz]
