Spin-Dynamics in the Carrier-Doped \( S = \frac{1}{2} \) Triangular-Lattice of Na\(_x\)CoO\(_2\)-yH\(_2\)O

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We probed the local electronic properties of the mixed-valent Co\(^{3+}\)\(-x\) triangular-lattice in Na\(_x\)CoO\(_2\)-yH\(_2\)O by \(^{59}\)Co NMR. We observed two distinct types of Co sites for \( x \geq \frac{1}{2} \), but the valence seems averaged out for \( x \sim \frac{1}{2} \). Local spin fluctuations exhibit qualitatively the same trend down to \( \sim 100 \) K regardless of the carrier-concentration \( x \), and hence the nature of the electronic ground state. A canonical Fermi-liquid behavior emerges below \( \sim 100 \) K only for \( x \sim \frac{1}{2} \), and water-intercalation enhances spin-fluctuations near \( T_c \).

\(^{59}\)Co nuclei have spin \( I = \frac{5}{2} \) (nuclear gyromagnetic ratio \( \gamma_n = 10.053 \) MHz/Tesla), and seven NMR transitions from the \( I_z = m \) to \( m + 1 \) state are expected for each different type of Co site \([13]\). We show representative lineshapes observed in the external magnetic field \( H_{ext} = 8 \) Tesla in Fig.2. All samples are single-crystals \([14]\) except for \( x = 0.72 \); the latter is a ceramic sample synthesized by the standard fast-heating method \([15]\), and magnetically aligned in styvac 1266. The lineshapes for \( x = 0.75, 0.72, 0.67, \) and 0.5 clearly establish the presence of at least two different types of \(^{59}\)Co NMR lines. They have different central resonance frequencies, e.g. \( \nu \sim 82 \) MHz at A’-sites and \( \sim 86 \) MHz at B’-sites in Na\(_{0.72}\)CoO\(_2\). In addition, the splitting, \( \nu_o \), between the central and satellite transitions due to nuclear quadrupole interaction with the local Electric-Field-Gradient (EFG) \([13]\) is different, e.g. \( \nu_o \sim 560 \) kHz at A’-sites and \( \nu_o \sim 560 \) kHz at B’-sites.

In the absence of hyperfine interactions with Co electrons, the \(^{59}\)Co NMR frequency would be \( \gamma_n H_{ext} = 80.4 \) MHz in \( H_{ext} = 8 \) Tesla. It is primarily the hyperfine magnetic field at each Co site that shifts the central resonance frequency \( \nu \sim \frac{1}{2}, \) and the former has a linear relation to the local magnetic susceptibility \( \chi_i^{spin} \) at the \( i \)-th Co site.

Generally, one can gain information on \( \chi_i^{spin} \) through the NMR Knight shift \( ^{59}K = (\nu - \nu_{ext} - \gamma_n H_{ext})/\gamma_n H_{ext} \) \([13]\) as presented in Fig.3 \([16]\), where

\[ ^{59}K = ^{59}K_{spin} + ^{59}K_{orb} = \sum_{i=0}^{6} H_i \chi_i^{spin} + ^{59}K_{orb}, \]  

where \( ^{59}K_{spin} \) is the spin contribution to the NMR Knight shift, \( H_i \) is the hyperfine interaction between the observed Co nuclear-spin and the Co electron-spin at the same site, and \( H_{1-5} \) represents the hyperfine interaction with electron spins at six nearest-neighbor Co sites. The orbital contribution is usually temperature-independent, and is estimated to be \( ^{59}K_{orb} = (2 \sim 3)\% \) below 250K based on preliminary \( K \) vs. \( \chi \) analysis \([17]\).
In Fig.4, we summarize $\frac{1}{T_1 T}$, the $^{59}$Co nuclear spin-lattice relaxation rate $\frac{1}{T_1}$ divided by temperature $T$. $\frac{1}{T_1 T}$ measures the low-frequency spectral weight of the local Co spin-fluctuations at the experimental frequency $\nu_n = 78 \sim 86$ MHz (depending on the particular transition we employ). Theoretically, the spin contributions to $\frac{1}{T_1 T}$ may be written using the imaginary part of the Co dynamical electron spin-susceptibility $\chi''(q, \nu_n)$ as [18],

$$\frac{1}{T_1 T} = \frac{2g_n^2 k_B}{g^2 \mu_B} \sum_q |A(q)|^2 \chi''(q, \nu_n)$$

where $A(q) = H_0 + \sum_{i=1,6} H_i e^{i q r_i}$ is the wave-vector $q$ dependent hyperfine form factor [18,19].

It is very important to realize that the spin contribution to the Knight shift show identical temperature dependence at two different Co sites in Na$_{0.72}$CoO$_2$ (A- and B-sites), as well as in Na$_{0.72}$CoO$_2$ (A' and B'-sites), despite the factor 6 to 8 difference in their magnitude. To underscore this point, in Fig.3 we plotted 6.05 $[$$^{59}K_a(A) - 1.1\%$] and 8.43 $[$$^{59}K_a'(A') - 1.6\%$] to match with $^{59}K_a$ at B- and B'-sites, respectively. In Fig.4, we also demonstrate that $\frac{1}{T_1 T}$ at B- and B'-sites show identical behavior with that at A- and A'-sites, respectively [20]. These results are not consistent with a simple phase-separation picture, and imply that the strongly magnetic B- and B'-sites are electronically coupled with the less magnetic A- and A'-sites, respectively. Furthermore, the ratio of the integrated NMR intensity between the strongly magnetic (B- and B'-sites) and less magnetic Co sites (A- and A'-sites) is consistent with $1 \sim x : x$ after careful corrections for the fast transverse relaxation time $T_2$ at the B- and B'-site. These findings strongly suggest that a charge-order leads to two mutually coupled Co sites: A- and A'-sites are less magnetic Co$^{3+}$-like ions with $S \sim 0$, while B- and B'-sites are strongly magnetic Co$^{4+}$-like ions with $S \sim \frac{1}{2}$.

In passing, notice that the saturation below $\sim 20$K of $^{59}K(A)$ and $^{59}K(B)$ (both in Fig.3) and SQUID data (not shown) in our Na$_{0.72}$CoO$_2$ is consistent with the SQUID data reported by Foo et al. [6] for their Na$_{0.75}$CoO$_2$ sample with accurately calibrated Na content. Our NMR and SQUID data showed no evidence for a bulk magnetic phase transition in this Na$_{0.75}$CoO$_2$ crystal. On the other hand, an earlier $\mu$SR work reported [7] a SDW phase transition below $\sim 20$K for $\sim 20\%$ volume fraction of a ceramic “Na$_{0.75}$CoO$_2$” sample prepared by fast heating method [15]. Interestingly, our Na$_{0.72}$CoO$_2$ ceramic sample, prepared by the same fast heating method, showed a continuous increase of SQUID data through $\sim 20$K following a Curie-Weiss behavior, and we found a variety of NMR signatures of a magnetic instability (e.g. a dramatic magnetic NMR line broadening of B'-line below $\sim 30$K, accompanied by temperature-dependent line-splitting of A'-line and Na NMR line [17]).

The Na-content of our ceramic sample was determined to be $0.72 \pm 0.02$ based on the c-axis lattice-constant, which is a monotonous function of Na content [6]. The complete details will be reported elsewhere [17].

In the antiferromagnetic phase Na$_{0.5}$CoO$_2$ [8], we also observed two types of Co NMR signals, E-sites and F-sites, with the integrated-intensity ratio 0.5:0.5. This is again consistent with a charge-order, but with a geometrical configuration different from Na$_{0.72}$CoO$_2$. Based on the magnitude of $\frac{1}{T_1 T}$, we may identify the E- and F-sites as the weakly and strongly magnetic Co sites, respectively. However, the valence of E- and F-sites may not be very different from the nominal averaged value of 3.5, as the difference in the magnitude of $\frac{1}{T_1 T}$ is at most $\sim 3$ and less dramatic than the case of Na$_{0.72}$CoO$_2$. We also found that the $^{59}$Co NMR satellite lineshape begins to show additional line-splitting below 88 K [17] where SQUID data exhibit a kink [6,14]. This suggests that the configuration of charge-order changes below 88 K. We note that a recent structural study at 3.5K suggests a zig-zag chain structure with two distinct Co sites [21]. A larger distribution in the magnitude of $\frac{1}{T_1 T}$ prevented us from defining it properly below $\sim 88$ K.

In metallic Na$_{0.67}$CoO$_2$, we observed only sharp D- and D'-lines above $\sim 30$ K, and their NMR properties were very similar. With decreasing temperature, broad C-sites emerge while the linewidth of the D- and D'-sites broaden. $\frac{1}{T_1 T}$ at D-sites is similar to that at the weakly magnetic A-sites in Na$_{0.75}$CoO$_2$. The ratio of the integrated-intensity between C- and D-, D'-sites is not consistent with 0.33:0.67 nor 0.67:0.33. The Co sites with magnetic moments may be missing in the Na$_{0.67}$CoO$_2$ lineshape due to their fast relaxation times.

In contrast with the results for $x \geq 0.5$, we have detected essentially only one class of $^{59}$Co NMR lines, G and G', in metallic Na$_{0.3}$CoO$_2$ at 4.2 K. $\nu_n$, $^{59}K$, and $\frac{1}{T_1 T}$ were nearly identical at both sites. Thus the valence of all Co ions in the ground state of $x \sim \frac{1}{3}$ doped Na$_{0.3}$CoO$_2$ seems averaged out. The special character of the electronic state at the $x \sim \frac{1}{3}$ doping may be induced by the geometry, as dynamic singlet formation would be energetically advantageous, see Fig.1(b). However, we cannot rule out the possibility that changes in the nature and extent of Na$^+$ vacancy order may be driving the changes of electronic properties across $x = 0.5$.

Now we turn our attention to the low-frequency Co spin-dynamics. One of the most interesting findings of this study is that $\frac{1}{T_1 T}$ shows qualitatively the same decrease with temperature down to $\sim 100$ K at all types of Co sites in all concentrations, regardless of the nature of the electronic properties below $\sim 100$ K and of the behavior of $^{59}K$ (i.e. the $q=0$ behavior of $\chi_{spin}$). For example: $\frac{1}{T_1 T}$ at A-, A', and D-sites decreases $\sim 30\%$ from 250K to 100K, where $\chi_{spin}$ shows an increase following a Curie-Weiss law; in $x = 0.3$, $\frac{1}{T_1 T}$ decreases $\sim 40\%$ in the same temperature range while
$\chi_{\text{spin}}^{x}$ also decreases. Even more interesting is the fact that $\chi_{\text{spin}}^{x}$ above 100 K at G-sites in Na$_{0.3}$CoO$_2$ is roughly the average of $\chi_{\text{spin}}^{x}$ at weakly magnetic E- and strongly magnetic F-sites in Na$_{0.5}$CoO$_2$. Furthermore, our preliminary results for water-intercalated, superconducting single-crystal Na$_{0.3}$CoO$_2$-1.3H$_2$O show identical $\chi_{\text{spin}}^{x}$ to that of Na$_{0.3}$CoO$_2$ above $\sim$100 K. The identical behavior indicates that the weaker inter-Co-layer coupling along the c-axis caused by water-intercalation does not affect the behavior of Co spin fluctuations above $\sim$100 K.

Thus our $\chi_{\text{spin}}^{x}$ results establish qualitatively the same suppression in the carrier-doped S = $\frac{1}{2}$ triangular-lattice with a comparable temperature scale(s) of the order of $\sim$100 K or higher, regardless of the carrier concentration $x$ and the inter-layer coupling. Interestingly, the intra-layer Co-Co exchange interaction is estimated to be $J = 140 \sim 280$ K for Na$_x$CoO$_{2-x}$H$_2$O by Wang et al. [3]. This reminds us that the Cu spin-lattice relaxation rate in the high-$T_c$ cuprate La$_{2-x}$Sr$_x$CuO$_{4}$ exhibits a universal value set entirely by the Cu-Cu exchange interaction $J \sim 1500$ K above $\sim 500$ K [22]. Perhaps $J$ is the single dominant parameter of $\chi_{\text{spin}}^{x}$ in the present case, too.

According to eq.(2), our $\chi_{\text{spin}}^{x}$ data imply that the q-integral of the low-frequency components of Co spin-fluctuations, weighted with the form factor $|A(q)|^2$, decreases with temperature down to $\sim$100 K. Since the total magnetic moment must be conserved, a possible scenario is that some spectral weight is being shifted to higher energies, in analogy with the pseudo-gap behavior in under-doped high $T_c$ cuprates [11]. Alternatively, the growth of the short-range order of Co spins below $T \sim J$ may result in the pile-up of a considerable fraction of the spectral weight of $\chi_{\text{spin}}^{x}(q, \nu_q)$ to a q-region where the form factor $|A(q)|^2$ happens to be small [23].

Surprisingly, despite qualitatively the same trend in spin dynamics for all concentrations $x$ down to $\sim$100 K, both $\chi_{\text{spin}}^{x}$ and $59K$ level off below $\sim$100 K only for $x = 0.3$, i.e. Korringa behavior [13]. This evidences for the emergence of a low-temperature canonical Fermi-liquid behavior for $x \sim \frac{1}{3}$ below $\sim$100 K, and is consistent with the emergence of $\sim T^2$ behavior of resistivity observed only for $x \sim \frac{1}{3}$ below $\sim$30K [6]. The large low-temperature specific-heat $\gamma \sim 10$ mJ/K$^2$-mol implies a substantial mass-enhancement by a factor 4$\sim$7 [24]. Quite remarkably, water-intercalation alters the temperature dependence of $\chi_{\text{spin}}^{x}$ for the $x \sim \frac{1}{3}$ doping below and only below $\sim$100 K. Somehow the reduced inter-layer coupling between Co sheets appears to introduce a new temperature (and/or energy) scale in the low temperature Fermi-liquid state in $x \sim \frac{1}{3}$.

To conclude, we demonstrated the presence of two-types of Co-sites in the carrier-doped Co triangular-lattice of Na$_x$CoO$_{2-x}$H$_2$O for $x \geq 0.5$ by probing the Co layers directly with $^{59}$Co NMR. The temperature dependences of $^{59}K$ and $\chi_{\text{spin}}^{x}$ suggest these sites are electronically coupled to each other. We also showed semi-quantitatively the same trend of spin-fluctuations above $\sim$100 K for a variety carrier concentrations from $x = 0.3$ to 0.75 with $y = 0$, and for varying strength of inter-layer coupling for a fixed $x = 0.3$ (i.e. $y = 0$ and $y = 1.3$). Our $\chi_{\text{spin}}^{x}$ results suggest the presence of a certain energy scale that shows little dependence on $x$ and $y$. We also demonstrated that a canonical Fermi-liquid behavior emerges at low temperatures only for $x \sim \frac{1}{3}$ but water-intercalation alters the low temperature spin dynamics.

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FIG. 1. (a) Schematics of the undoped \((x = 0)\) \( \text{Co}^{4+} \) triangular-lattice with \( S = \frac{1}{2} \). When the nearest-neighbor exchange interaction \( J \) tends to align two \( S = \frac{1}{2} \) spins (#1 and #2) in an anti-parallel configuration, frustration would result for spin #3. (b) For finite values of \( x \) (\( x = \frac{1}{3} \) in this panel), extra electrons could help local-singlet formation, and alter spin-correlations dramatically.

FIG. 2. \(^{59}\)Co NMR lineshape with \( H_{\text{ext}} = 8 \) Tesla applied along a-axis. (The lineshapes for \( \text{Na}_0.72\text{CoO}_2 \) and \( \text{Na}_0.3\text{CoO}_2-1.3\text{H}_2\text{O} \) were obtained with \( H_{\text{ext}} \) applied within ab-plane for aligned ceramics and single crystals, respectively. The lineshapes for \( x=0.75 \) and 0.72 are corrected for \( T_2 \).) The arrows indicate the central transition \( \nu_{-\frac{1}{2},+\frac{1}{2}} \) at various Co sites. For \( x=0.75, 0.72, \) and 0.67, \(^{23}\)Na NMR line was superposed above \( \sim 88 \) MHz. Some of the furthest satellite transitions are not shown.

FIG. 3. The \(^{59}\)Co NMR Knight shifts \(^{59}K_a\) at B, B’, D, F, G, and H-sites. (Note that \(^{59}K_{\text{orb}} \sim 2-3\% \) is not subtracted.) Also plotted are \(^{59}K_c\) measured at A- and A’-sites scaled to match with B- and B’-sites (see the main text).

FIG. 4. The temperature dependence of \( \frac{1}{T_1T} \).
(a) $x=0$

(b) $x=1/3$

frustration

Co$^{3+}$ (S=0)
singlet
$D (\nu_a \sim 1.4 \text{MHz})$
$C (\nu_a \sim 2 \text{MHz})$
$E (\nu_a \sim 2.8 \text{MHz})$
$F (\nu_a \sim 4 \text{MHz})$
$G, G' (\nu_a \sim 4 \text{MHz})$
$H (\nu_{ab} \sim 1.8 \text{MHz})$
$B (\nu_a \sim 600 \text{kHz})$
$B' (\nu_{ab} \sim 650 \text{kHz})$
$A' (\nu_{ab} \sim 560 \text{kHz})$
$A (\nu_a \sim 250 \text{kHz})$
$\text{Na}_0.3 \text{-} 1.3 \text{H}_2\text{O}$
$\text{Na}_0.67$
$\text{Na}_0.72$
$\text{Na}_0.75$
$\text{Na}_0.5$
$\text{Na}_0.3$
$4.2 \text{K}$
$21 \text{K}$
$77 \text{K}$
$100 \text{K}$
