Hydration-induced anisotropic spin fluctuations in Na$_x$CoO$_2$·1.3H$_2$O superconductor

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received 11 August 2008; accepted in final form 3 November 2008
published online 16 December 2008

PACS 74.25.Jb – Electronic structure
PACS 74.70.-b – Superconducting materials
PACS 74.25.Nf – Response to electromagnetic fields (nuclear magnetic resonance, surface impedance, etc.)

Abstract – We report $^{59}$Co NMR studies in single crystals of the cobalt oxide superconductor Na$_{0.42}$CoO$_2$·1.3H$_2$O ($T_c=4.25$ K) and its parent compound Na$_{0.42}$CoO$_2$. We find that both the magnitude and the temperature ($T$) dependence of the Knight shifts are identical in the two compounds above $T_c$. The spin-lattice relaxation rate (1/$T_1$) is also identical above $T_0\sim 60$ K for both compounds. Below $T_0$, the unhydrated sample is found to be a non-correlated metal that well conforms to the Fermi liquid theory, while spin fluctuations develop in the superconductor. These results indicate that water intercalation does not change the density of states at the Fermi level or the carrier density but its primary role is to bring about spin fluctuations. Our result shows that, in the hydrated superconducting compound, the electron correlation is anisotropic. Namely, the spin fluctuation around the finite wave vector is much stronger along the $a$-axis direction than that along the $c$-axis direction.

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The hydrated cobalt oxide superconductor Na$_x$CoO$_2$·1.3H$_2$O has attracted much attention in the past few years [1]. This compound bears similarities to the high transition temperature ($T_c$) copper oxides in that it has a layered crystal structure and contains a transition metal element that carries a spin of $\frac{1}{2}$. Moreover, Co forms a triangular lattice rather than a square lattice as in the cuprates, which may lead to new physics associated with spin frustrations. Therefore, insights into this new class of superconductors are expected to shed light on the mechanism of high-$T_c$ superconductivity and may also have impact on other strongly correlated electron systems.

Nuclear quadrupole resonance (NQR) has revealed the unconventional nature of the superconductivity; the spin-lattice relaxation rate $1/T_1$ shows no coherence peak just below $T_c$, which is suggestive of a non–s-wave superconducting state [2]. The absence of the coherence peak is universal irrespective of the Na content or $T_c$ value [3,4]. At low temperatures, $1/T_1$ follows a $T^3$ variation down to a temperature as low as $\frac{T}{T_c}$ [3,4], which indicates the existence of nodes (zeroes) in the gap function. The knowledge about spin-pairing symmetry was obtained from Knight shift [5,6]. 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 appears to be of nodal $d$-wave symmetry [7,8].

In the normal state, the quantity $1/T_1 T$ does not follow the Korringa relation for a non-correlated metal, but increases with decreasing temperature, which indicates electron correlations [2]. $^{59}$Co Knight shift measurement shows that the uniform spin susceptibility decreases with decreasing temperature and becomes a constant below $T \sim 60$ K before superconductivity sets in, along both $a$- and $c$-axis directions [5]. This result strongly suggests that the spin correlations are of antiferromagnetic (AF) origin. It is worth noting that such AF-like spin fluctuations increase with decreasing Na content, and become strongest at $x \sim 0.26$ where $T_c$ is the highest [3].

In cuprates, isotropic spin fluctuations have been widely assumed, which successfully explained the observed spin dynamics [9]. However, the detailed characters of the spin fluctuations, for example, its anisotropy between the

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α-axis direction and the c-axis-direction, is unknown in the cobaltates. This is due mainly to the difficulty in growing large-size single crystals. The other outstanding issue in the cobaltate is the role of water intercalation in achieving superconductivity. In spite of efforts [10–14], it remains unclear. Also, researches on unhydrated Na$_x$CoO$_2$ compounds have so far focused on high Na concentrations with $x > 0.5$; the electronic state of Na$_x$CoO$_2$ ($x < 0.5$), the parent of the superconductor, is poorly understood. Previous NQR or NMR measurements did not provide detailed information on the electron correlations [15,16].

In this paper, we address these issues through comparative studies of the Knight shift and $1/T_1$ on the hydrated superconductor Na$_{0.42}$CoO$_2$·1.3H$_2$O and unhydrated Na$_{0.42}$CoO$_2$ single crystals. We find that Na$_{0.42}$CoO$_2$ is a conventional metal that well conforms to the Fermi liquid theory for non-correlated electrons, and that hydration does not alter the density of states (DOS) or carrier concentration. The principal role of hydration is to bring about spin fluctuations which are found to be highly anisotropic. The anisotropic spin correlations appear to be essential for the superconductivity.

The single crystals of Na$_{0.42}$CoO$_2$ and Na$_x$CoO$_2$·1.3H$_2$O used in this study (2 mm × 4 mm × 0.1 mm) were grown by the traveling solvent floating zone (TSFZ) method followed by hydration for the later compound, as described in previous publications [17,18]. The $^{59}$Co (nuclear spin $I = 7/2$) NMR spectra were taken by changing the external magnetic field ($H$) at a fixed rf frequency and recording the echo intensity step by step. The $1/T_1$ was measured at the lower first satellite (3/2 ↔ 1/2 transition) for $H \parallel c$, and at the central peak (1/2 ↔ −1/2 transition) for $H \parallel a$. The value of $1/T_1$ was extracted by fitting the nuclear magnetization to the theoretical curve of Narath [19].

Figure 1 shows a typical example of the NMR spectra for both samples with the magnetic field applied along the c- ($H \parallel c$) and α-axis ($H \parallel a$). For $H \parallel c$, a sharp central transition line accompanied by six satellites due to the nuclear quadrupole interaction is observed. In Na$_{0.42}$CoO$_2$, the principal NQR frequency tensor $ν_c = 0.47$ MHz and the asymmetric parameter $η = 0$. In Na$_{0.42}$CoO$_2$·1.3H$_2$O, $ν_c = 3.99$ MHz and $η$ is finite, as can be seen from the spectrum.

Figure 2 shows the temperature dependence of the Knight shift ($K$) for both hydrated and unhydrated samples, $K_a$ with the field applied along the α-axis, and $K_c$ with the field applied along the c-axis. $K_c$ was determined from the central peak, which agrees well with that determined from the midpoint between the two first satellites. $K_a$ was determined from the central peak by taking into account the shift due to the nuclear quadrupole interaction [20], for both samples and along both crystal axis directions, the Knight shift decreases with decreasing temperature down to $T_0 \sim 60$ K, and then becomes a constant at lower temperatures. The most striking feature is that both the magnitude and the temperature dependence of the Knight shifts are identical for the two compounds, except the drop of $K_{a,c}$ at the superconducting transition in the hydrated sample.

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1 Here we take the opportunity to correct an error in calculating the effect of nuclear quadrupole interaction which appeared in the data of $K_a$ ($T \geq 100$ K) of ref. [5].
The Knight shift consists of contributions from the spin susceptibility, \( K_s \), and from the orbital susceptibility (Van Vleck susceptibility), \( K_{\text{orb}} \) [20],

\[
K = K_s + K_{\text{orb}},
\]

with \( K_{\text{orb}} \) being \( T \)-independent. \( K_s(T) \) and \( K_{\text{orb}} \) are, respectively, related to the spin susceptibility \( \chi_s \) and orbital susceptibility \( \chi_{\text{orb}} \) as

\[
K_s(T) = A_{hf} \chi_s(T),
\]

\[
K_{\text{orb}} = A_{\text{orb}} \chi_{\text{orb}},
\]

where \( A_{hf} \) is the hyperfine coupling constant between the nuclear and the electron spins, and \( A_{\text{orb}} = 2(1/r^3) \) with \( \langle \cdots \rangle \) denoting an average over the Co-3d orbit. Therefore, the temperature dependence of \( K \) is due to the spin susceptibility that decreases with decreasing \( T \), which is a common feature seen in low hole-doped [21] and electron-doped [22] cuprate superconductors. In analogy to the cuprates, this phenomenon may arise from low dimensionality of an antiferromagnetic spin system, or may be ascribed to some sort of pseudogap [23,24]. However, unlike the cuprates, the seemingly pseudogap is unrelated to superconductivity in the cobaltate.

Since \( \chi_s \) is proportional to the DOS at the Fermi level, the identical Knight shift in the two compounds therefore indicates that the DOS is the same in hydrated and unhydrated samples. Note that, in the case of Na doping that adds electrons to the Co \( t_{2g} \) orbit, DOS is sensitive to the Na content [3]. Therefore, the present result indicates that water intercalation does not alter the carrier concentration, which is at variance with the early suggestion that carrier concentration may change after hydration [12,13]. The first-principle calculation has predicted that water intercalation has no effect on the band structure other than making the system more two dimensional [10,11], which agrees with our finding.

Next, we estimate the hyperfine coupling constant and separate the spin and orbital susceptibilities. In fig. 3, the Knight shift for the unhydrated sample is plotted as a function of DC susceptibility of which the data for \( H \parallel c \) has been published previously [18]. The diamagnetic susceptibility due to closed shells of Na, Co, and O was estimated to be \(-5.7 \times 10^{-5} \text{emu/mol}[25]\), from which the slope of \( A_{\text{orb}} \) was drawn. Here, \((1/r^3) = 5.4 \text{ a.u.}\) is adopted, which is 80% theoretical value for the Co\(^{3+}\) ion [26]. From this \( K-\chi \) plot, the hyperfine coupling constant is extracted as \( A_{hf}^a = 124 \pm 20 \text{kOe/\(\mu_B\)} \) and \( A_{hf}^c = 112 \pm 10 \text{kOe/\(\mu_B\)} \), respectively. The orbital part of the shift and susceptibility are \( K_{\text{orb}}^a = 2.96 \pm 0.1\%\), \( \chi_{\text{orb}}^a = (2.49 \pm 0.1) \times 10^{-4} \text{emu/mol-Co} \) and \( K_{\text{orb}}^c = 1.72 \pm 0.04\%\), \( \chi_{\text{orb}}^c = (1.44 \pm 0.03) \times 10^{-4} \text{emu/mol-Co} \). A previous study using aligned powders, based on a method different from the \( K-\chi \) plot, has given similar \( K_{\text{orb}}^c\); the values obtained there are 10\% larger than ours [14]. It is remarkable that, within the experimental uncertainty, the hyperfine coupling constant is nearly isotropic. For the hydrated sample, the DC susceptibility is contaminated by a Curie upturn, due to the magnetic impurity arising from partial decomposition during the hydration process [27], which prevents one to do the \( K-\chi \) plot. Since the Knight shift is identical to the unhydrated compound, and so is the \( 1/T_1 T \) at \( T \geq 60 \text{ K} \) (see below), it is reasonable to expect the same hyperfine coupling constant for the hydrated sample.

Finally, we evaluate the spin correlations. Figure 4 shows the temperature dependence of \( 1/T_1 T \) above 4.2 K for \( H \parallel c \) and \( H \parallel a \) in both hydrated and unhydrated samples. Again, it is striking that, above \( T_0 = 60 \text{ K} \), \( 1/T_1 T \) is identical for both compounds. The two compounds share
the same feature that $1/T_1 T$ decreases with decreasing $T$ down to $T_0 \sim 60\text{K}$ in both directions. Below $T_0$, $1/T_1 T$ is constant for the unhydrated sample, which indicates that the electronic correlations are weak. In fact, the Korringa ratio \[ S = T_1 T K^2 = \frac{4\pi k_B}{\hbar} \left( \frac{\gamma_0}{\gamma_c} \right)^2, \]
which is unity for a free-electron system, is $0.65 \pm 0.3$, being close to the value for Pb or Be metals. Therefore, the unhydrated Na$_{0.42}$CoO$_2$ is a conventional metal that well conforms to the Fermi liquid theory. This is further corroborated by the good agreement between the calculated DOS by LDA (local density approximation) and our estimated value. The spin susceptibility $\chi''_n$ is extracted from fig. 3 to be $1.91 \times 10^{-4}\text{emu/mol\cdot Co}$ at 100 K, which yields the DOS at the Fermi level,
\[ N(E_F) = \frac{\chi_s}{2\mu_B^2} = 2.95 \text{ state/eV}. \]
This is very close to the LDA value of 4.4 state/eV [28].

In contrast, $1/T_1 T$ increases with decreasing $T$ for the hydrated sample in both directions, indicating strong electron correlations. In a general form, $1/T_1 T$ is written as
\[ \frac{1}{T_1 T} = \frac{\pi k_B \gamma_n^2}{(\gamma_c \hbar)^2} \sum_q A_{hf}^2 \frac{\chi''_n(q, \omega)}{\omega}, \]
where $\chi''_n(q, \omega)$ is the imaginary part of the dynamical susceptibility perpendicular to the applied field, and $\omega$ is the NMR frequency.

If one assumes that there is a peak around a finite wave vector $Q$ (due to spin fluctuation), then one may have the following approximation:
\[ \frac{1}{T_1 T} = \left( \frac{1}{T_1 T} \right)_0 + \left( \frac{1}{T_1 T} \right)_Q, \]
\[ \left( \frac{1}{T_1 T} \right)_Q = \frac{\pi k_B \gamma_n^2}{(\gamma_c \hbar)^2} \sum_{q \approx Q} A_{hf}^2 \frac{\chi''_n(q, \omega)}{\omega}, \]
where $(1/T_1 T)_0$ is the contribution from wave vectors around $Q$, while $(1/T_1 T)_Q$ denotes the contribution that is proportional to the squared DOS at the Fermi level. The unhydrated sample becomes a conventional metal, while the spin correlation develops upon decreasing temperature in the hydrated sample. Therefore, the water intercalation is to bring about the antiferromagnetic-like spin correlations, perhaps through modifying the Fermi surface as to favor nesting conditions. Angle-resolved photoemission spectroscopy is encouraged to compare the Fermi surface of hydrated and unhydrated compounds. The insertion of two layers of water molecules largely separates the CoO$_2$ layers, and it is likely because of the hydrogen bonding [29,30] that makes water particularly suitable as a spacer than others.

![Fig. 5: (Color online) $T$-dependence of the susceptibility around $Q$. The filled circles represent $\sum_{q \approx Q} \chi''_n(q)$, while the open circles for $\sum_{q \approx Q} \chi''_c(q)$.](image)

We estimate the anisotropy of the spin fluctuations in the superconductor by analyzing $\sum_{q \approx Q} \chi''_n(q)$. $(1/T_1 T)_Q$ is obtained by subtracting $(1/T_1 T)_0$ for the unhydrated sample from the observed $1/T_1 T$. From the symmetry of the crystal structure, we have
\[ \left( \frac{1}{T_1 T} \right)_Q^c = \frac{2\pi k_B \gamma_n^2}{(\gamma_c \hbar)^2} \sum_{q \approx Q} (A_{hf}^c)^2 \chi''_n(q), \]
\[ \left( \frac{1}{T_1 T} \right)_Q^a = \frac{\pi k_B \gamma_n^2}{(\gamma_c \hbar)^2} \sum_{q \approx Q} \left[ (A_{hf}^a)^2 \chi''_n(q) + (A_{hf}^c)^2 \chi''_c(q) \right]. \]

By making use of nearly isotropic hyperfine coupling constant, the anisotropy of the susceptibility around $Q$ is obtained as shown in fig. 5. As can be seen in the figure,
\[ \sum_{q \approx Q} \chi''_a(q) \geq 3 \sum_{q \approx Q} \chi''_c(q), \]
just above $T_c$. Namely, the spin fluctuations there in the $a$-axis direction are more than three times stronger than along the $c$-axis direction. Thus, the highly anisotropic spin fluctuations turn out to be the most important ingredient of the superconductor.

In conclusion, we have presented $^{59}$Co-NMR measurements and analysis on the hydrated and unhydrated cobalt oxide single crystals. The unhydrated compound Na$_{0.42}$CoO$_2$ is found to be a non-correlated metal. After water intercalation, the antiferromagnetic-like spin fluctuations develop but there is no change in the DOS at the Fermi level. Therefore, the primary role of water intercalation is to make the system more two dimensional and brings about spin fluctuations. The spin correlations in the superconductor is anisotropic; they are stronger in the
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α-axis direction than along the c-axis direction by a factor of 3, which is quite different from the cuprate case. These new results and insights provide a foundation for understanding the mechanism of superconductivity in cobalt oxides.

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We thank P. C. Dai, I. Eremin and S. Kawasaki for useful discussions. This work was supported in part by research grants from MEXT and JSPS.

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