Unconventional Superconductivity and Electron Correlations in the Cobalt Oxyhydrate $Na_{0.35}CoO_2 \cdot yH_2O$ from Nuclear Quadrupole Resonance

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We report a careful ^{59}Co nuclear quadrupolar resonance measurement on the recently discovered cobalt oxyhydrate $Na_{0.35}CoO_2 \cdot yH_2O$ superconductor from $T = 40$ K down to 0.2 K. We find that in the normal state the spin-lattice relaxation rate $1/T_1$ follows a Curie-Weiss type temperature (T) variation, $1/T_1T = C/(T - \theta)$, with $\theta = -42$ K, suggesting two-dimensional antiferromagnetic spin correlations. Below $T_c = 3.9$ K, $1/T_1$ decreases with no coherence peak and follows a T^n dependence with $n \simeq 2.2$ down to $\sim$2.0 K but crosses over to a $1/T_1 \propto T$ variation below $T = 1.4$ K, which suggests non-s-wave superconductivity. The data in the superconducting state are most consistent with the existence of line nodes in the gap function.

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The recent discovery of superconductivity in layered cobalt oxyhydrate $Na_{0.35}CoO_2 \cdot yH_2O$ [1] has generated new excitement in the condensed matter physics community, since it suggests a possible new route to find high-T_c superconductivity and also demonstrates the richness of physics in layered transitional metal oxides. The compound consists of two-dimensional CoO_2 layers separated by insulating blocks of Na^{+1} and H_2O molecules, resembling the layered structure of copper-oxide high-T_c superconductors. Because of the octahedral crystal environment, Co^{+4} is in the low spin state ($S = 1/2$), and the compound $Na_{0.35}CoO_2 \cdot yH_2O$ is considered as a system in which 35% electrons are doped to a spin 1/2 triangular lattice. Insight from investigations of this compound is expected to shed light on the mechanism of cuprate superconductors. Several experiments [2–6] have been conducted to investigate its physical properties and many theoretical proposals on the symmetry of the superconductivity [7–13] have been put forward.

In this Letter, we report a careful measurement using ^{59}Co nuclear quadrupolar resonance (NQR) on the normal and superconducting states of $Na_{0.35}CoO_2 \cdot yH_2O$. In the normal state, it was found that the spin-lattice relaxation rate $1/T_1$ divided by temperature (T) follows a Curie-Weiss law of $1/T_1T \propto 1/(T + 42)$, suggesting the two-dimensional antiferromagnetic spin correlations. In the superconducting state, $1/T_1$ decreases below $T_c = 3.9$ K, with no coherence peak and follows a power law of T^n with $n \simeq 2.2$ down to $\sim$2.0 K but crosses over to a $1/T_1 \propto T$ variation below $T = 1.4$ K, which suggests unconventional superconductivity. These results show that the layered Co compound bears a close resemblance to the copper-oxide high-T_c superconductors without a full gap.

The $Na_{0.35}CoO_2 \cdot yH_2O$ powder was synthesized as described in Refs. [1,14]. The x-ray spectrum shows the reflections of the hexagonal space group $P63/mmc$ with lattice parameters $a = 2.820$ Å and $c = 19.593$ Å [3]. T_c was found to be 3.9 K from the ac susceptibility measured by using the *in situ* NQR coil. NQR measurements were carried out using a phase-coherent spectrometer. Measurements below 1.4 K were performed by using a ^{3}He/^{4}He dilution refrigerator and a small amplitude of radio-frequency pulses. The $1/T_1$ of ^{59}Co was measured by the saturation-recovery method. Three NQR transition lines arising from spin $I = 7/2$ of ^{59}Co were found at 4.78, 8.05z, and 12.30 MHz, which corresponds to $\nu_Q = 4.12$ MHz and the asymmetry parameter $\eta = 0.223$. Here ν_Q and η are defined as $\nu_Q \equiv \nu_z = \frac{3}{2I(2I-1)h} e^2 Q \frac{\partial^2 V}{\partial z^2}$, and $\eta = |\nu_x - \nu_y|/\nu_z$, with Q being the nuclear quadrupolar moment, $I = 7/2$ being the nuclear spin, and $\frac{\partial^2 V}{\partial \alpha^2}$ ($\alpha = x, y, z$) being the electric field gradient at the position of the nucleus [15]. The inset of Fig. 1 shows the $\pm 3/2 \leftrightarrow \pm 5/2$ transition line at whose peak T_1 was measured. The spectrum has a full width at half maximum of 0.3 MHz. The main panel of the figure shows the typical nuclear magnetization $M(t)$ that is excellently fitted to the theoretical curve $\frac{M_0 - M(t)}{M_0} = 0.095 \exp(-3t/T_1) + 0.095 \times \exp(-90.5t/T_1) + 0.819 \exp(-19t/T_1)$ [16], with a unique T_1 component. Both the fairly narrow NQR spectrum and the single-component nuclear magnetization curve indicate good quality of the sample.

Figure 2 shows the temperature dependence of $1/T_1$. Below T_c, $1/T_1$ decreases with no coherence (Hebel-Slichter) peak, and follows a power-law dependence of T^n. If one fits the data for $3.8\ \text{K} \geq T \geq 2.0$ K, one gets an $n \simeq 2.2$. This is strong evidence for non-s-wave superconductivity. For an s-wave, isotropic gap, $1/T_1$ shows a coherence peak just below T_c and follows an exponential temperature dependence at lower temperature. The most immediate explanation of our data is the possible existence of line nodes in the gap function as in d- or p-wave

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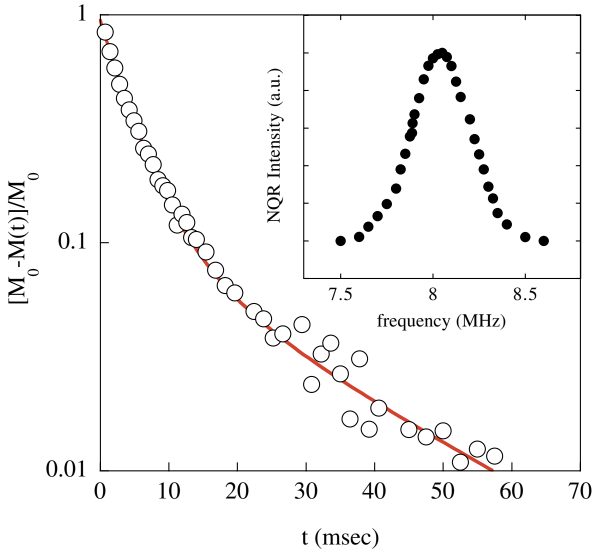

FIG. 1 (color online). ^{59}Co nuclear magnetization decay curve at $T = 1.7$ K fitted uniquely by the expected theoretical curve (see text). The inset shows the NQR line shape ($\pm 3/2 \leftrightarrow \pm 5/2$ transition) at whose peak T_1 was measured.

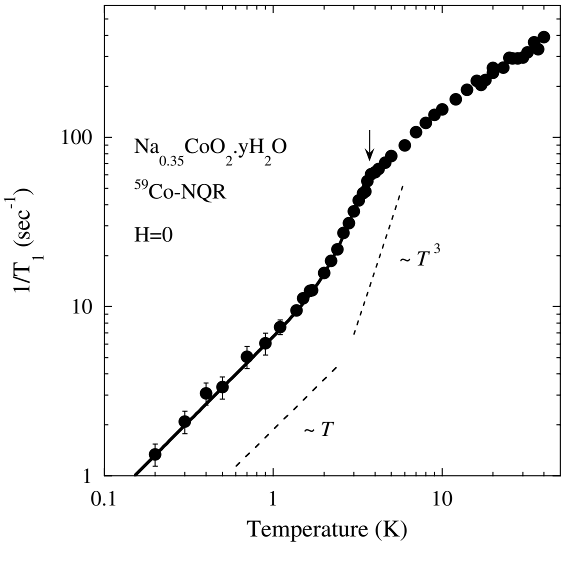

FIG. 2. $1/T_1$ as a function of temperature. The curve below T_c is a calculation for the line-nodes gap function in the presence of impurity scattering (see text for detail).

superconductors, where an energy (E) linear density of states (DOS) at low E results in a T^n ($n = 3$) dependence of $1/T_1$. In the presence of disorder/impurity scattering, the exponent n could appear smaller than 3 as shown shortly. For d- or p-wave superconductivity, the "coherence factor" [17] due to isotropic pairing is absent; therefore the enhancement of $1/T_1$ just below T_c is greatly reduced. If there is no strong divergence of the DOS at $E = \Delta_0$ (Δ_0 is the maximum gap amplitude), there is no peak seen just below T_c. The slight retarded (by 0.1 K in temperature; see the arrow in Fig. 2) drop of $1/T_1$ below T_c^{χ} suggests that bulk superconductivity sets in at a temperature 0.1 K below the onset of diamagnetism seen in the susceptibility, as the case that has been encountered previously in some superconductors. For example, in the heavy fermion superconductor CeIrIn$_5$, although the susceptibility shows a superconducting onset at ~0.6 K [18], $1/T_1$ starts to drop only at 0.4 K [19]. This also happens in the isostructure heavy fermion compound CeRhIn$_5$ in the vicinity of magnetic order where $1/T_1$ shows a rapid decrease at a temperature far below the susceptibility onset temperature [20].

At lower temperatures, the decrease of $1/T_1$ becomes more gradual, and below $T = 1.4$ K, $1/T_1$ becomes proportional to T down to $T = 0.2$ K. In the case of nodal superconductivity, this result can then be interpreted as due to disorder or impurity that acts as pair breaker [21,22], as seen in many strongly correlated superconductors [23]. T_1 in the superconducting state can be expressed as $\frac{T_1(T=T_c)}{T_1} = \frac{2}{k_B T_c}\int(\frac{N_s(E)}{N_0})^2 f(E)[1 - f(E)]dE$, where $N_s(E)/N_0 = E/\sqrt{E^2 - \Delta^2}$ with N_0 being the DOS in the normal state and $f(E)$ being the Fermi function. The solid curve below T_c shown in Fig. 2 is a calculation assuming line nodes in the gap function, $\Delta = \Delta_0 \cos 2\theta$, with $\Delta_0 = 2.6 k_B T_c$ and a residual DOS ($N_{\rm res}$) due to impurity (disorder) scattering [22], $N_{\rm res} = 0.65 N_0$. The curve fits the data quite well. The deviation from the T^3 law at quite a high temperature is hence an effect of the large $N_{\rm res}$ that produces a large value of $1/T_1 \propto T$. The gap function of $\Delta = \Delta_0 \cos\theta$, with $\Delta_0 = 3.0 k_B T_c$ and $N_{\rm res} = 0.65 N_0$, can also fit the data. It should be emphasized that s-wave or extended s-wave superconductivity in the presence of impurity scattering leads to a fully opened gap [24], which is inconsistent with our results. Finally, we note that it was recently shown that line-nodes gap ($d_{x^2-y^2}$ gap) is possible in the anisotropic triangular lattice Hubbard model at half filling [25,26].

The clean chiral d-wave or p-wave superconductivity with a full gap [7–11] does not find immediate agreement with our data. On the other hand, the presence of disorder or impurity may fill up the gap, rendering the low-E DOS. Very recently, Wang and Wang calculated the effect of a single impurity/interface on $d_{x^2-y^2} + id_{xy}$ or $p_x + ip_y$ superconductivity [27], and they found that the impurity-induced subgap states tend to cover the gap regime of the chiral superconductivity. However, it would be a coincidence that an E-linear DOS shows up in such a case. Measurements in samples with different degrees of defect or Na concentration may help settle this issue. On the theoretical side, a detailed calculation of the spatially averaged DOS for finite concentration of impurity is desirable for comparison with experiments.

Next, we turn to the normal state. In Fig. 3 is shown the temperature variation of $1/T_1T$. There, it is seen that the $1/T_1T$ increases with decreasing T. This is a feature not

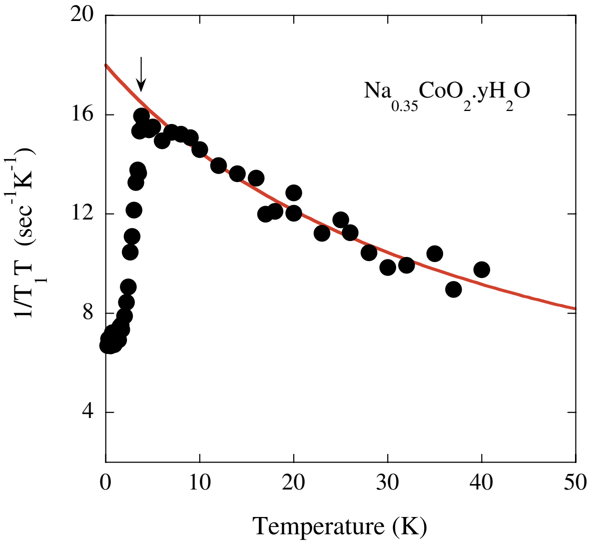

FIG. 3 (color online). $1/T_1T$ develops with decreasing temperature. The curve above $T = 10$ K is a fitting to $C/(T + \theta)$.

seen in conventional metals where $1/T_1T$ is a constant, but resembles the Cu relaxation in cuprate high-T_c superconductors with layered square lattices. Above $T = 10$ K, $1/T_1T$ follows a Curie-Weiss law, namely, $1/T_1T = \frac{C}{T-\theta}$, with $\theta = -42$ K and $C = 750\ \mathrm{sec}^{-1}$. We interpret this feature as arising from two-dimensional antiferromagnetic fluctuations. For antiferromagnetically correlated itinerant electron systems, the staggered spin susceptibility is shown to follow a Curie-Weiss type temperature variation [28,29]. Since $1/T_1T$ probes the dynamical susceptibility averaged over the momentum space, it is a good probe of electron correlation, as has been proven in cuprate superconductors. In the present case, although ferromagnetic correlation is present for large Na concentration ($x = 0.7$) [30], antiferromagnetic coupling was found in low concentration of Na [31] and also in $Na_{0.35}CoO_2 \cdot yH_2O$ [1].

The unconventional superconductivity developed with the background of antiferromagnetic spin correlations in $Na_xCoO_2 \cdot yH_2O$ bears close similarities to the case of high-T_c cuprates and suggests the importance of electron correlations in the occurrence of the superconductivity in the layered electron systems. In this regard, the lower T_c of the cobaltate may be ascribed to its antiferromagnetic exchange energy that is smaller by 1 order of magnitude than in cuprates [31].

Finally, we comment on two NMR-NQR papers [32,33] that report a finding of a coherence peak, of which we became aware after completing this work. We have found that no coherence peak is present as well in a sample with different content of Na and with a $T_c =$ 4.8 K, which indicates that the unconventional nature, i.e., the lack of the coherence peak just below T_c, is an intrinsic feature of this class of superconductors, irrespective of T_c. We believe that the coherence peak reported in [32,33] is due to inadequate T_1 measurements. First, the NMR signal assignment by Waki *et al.* [32] is likely incorrect. The peak these authors thought to be the Co $-1/2 \leftrightarrow 1/2$ transition shows much longer T_1 (longer by 2 orders of magnitude) than that correctly measured by NQR and that measured at other NMR peaks which we confirmed to show a quite consistent result with NQR. Second, these authors did not fit the nuclear magnetization curve to the rate equation to extract an adequate T_1 value for that, likely spurious, signal. In Ref. [33], on the other hand, although Kobayashi *et al.* also measured T_1 by NQR, the procedure to extract T_1 is rather complex; they assumed that there are two components of T_1 contribution.

In conclusion, we have presented a ^{59}Co NQR study on the recently discovered cobalt oxyhydrate $Na_{0.35}CoO_2 \times yH_2O$ superconductor from $T = 40$ K down to 0.2 K. In the normal state the spin-lattice relaxation rate $1/T_1$ follows a Curie-Weiss type temperature (T) variation, $1/T_1T = C/(T - \theta)$, with $\theta = -42$ K, suggesting two-dimensional antiferromagnetic spin correlations. Below $T_c = 3.9$ K, $1/T_1$ decreases with no apparent coherence peak and follows T^n ($n \sim 2.2$) dependence down to 2.0 K. At lower temperatures, the decrease of $1/T_1$ becomes more gradual, and a $1/T_1 \propto T$ variation is observed below $T = 1.4$ K. These data suggest non-s-wave superconductivity and are most consistent with the line-nodes gap model in the presence of scattering by disorder or impurity. None of the current theories proposed for the gap symmetry of the CoO_2-based superconductor finds immediate agreement with our results, and we hope our experiment will stimulate further theoretical works.

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