Superconductivity of the $Sr_2Ca_{12}Cu_{24}O_{41}$ Spin-Ladder System: Are the Superconducting Pairing and the Spin-Gap Formation of the Same Origin?

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Pressure-induced superconductivity in a spin-ladder cuprate $Sr_2Ca_{12}Cu_{24}O_{41}$ has not been studied on a microscopic level thus far although the superconductivity was already discovered in 1996. We have improved the high-pressure technique using a large high-quality crystal, and succeeded in studying the superconductivity using ^{63}Cu nuclear magnetic resonance. We found that the anomalous metallic state reflecting the spin-ladder structure is realized and the superconductivity possesses an s-wave-like character in the meaning that a finite gap exists in the quasiparticle excitation: At a pressure of 3.5 GPa, we observed two excitation modes in the normal state from the relaxation rate T_1^{-1}. One gives rise to an activation-type component in T_1^{-1}, and the other T-linear component linking directly with the superconductivity. This gapless mode likely arises from free motion of holon-spinon bound states appearing by hole doping, and the pairing of them likely causes the superconductivity.

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$Sr_{14-x}Ca_xCu_{24}O_{41}$ ($x = 11.5$–13.5) is a spin-ladder system in which a superconducting state is realized by applying pressure [1]. The system possesses a structural unit of the Cu_2O_3 two-leg ladder [2], and holes are transferred from the CuO_2 chain unit by substituting Ca for Sr. The dopant hole density can be controlled over a wide range from 0.07 ($x = 0$) to 0.24 ($x = 14$) per ladder Cu [3]. It is known from theoretical investigations that the ground state of undoped system is a quantum spin liquid and this state persists even in the highly doped region [4–6]. The spin gap has been observed by a number of works in the present ladder system. The decrease of the spin gap for the Ca substitution was observed in the NMR measurements [7–9], although no change was observed in the neutron scattering [10]. The relationship and interplay between the spin gap and the superconductivity in the hole-doped ladder system is of central concern [4–6,11] as is the case with high-T_c cuprates in the underdoped region [12].

The superconducting state is realized when a high pressure of 3–8 GPa is applied for highly doped compounds ($x \geq 10$) [3]. Pressure plays a role of stabilizing the metallic state and suppressing anisotropy within the ladder plane. In fact, the temperature (T) dependence of the resistivity in the direction perpendicular to the plane ρ_c which is insulating at low pressures turns to be metallic as pressure increases [13,14]. The ratio of the resistivities along the rungs and the legs, ρ_a/ρ_c, goes up to 80 at ambient pressure, but is reduced below 30 at 3.5 GPa [13].

The superconductivity has been studied on a macroscopic level by the resistivity and ac susceptibility measurements because these measurements are performable with a small amount of sample, and the cubic-anvil pressure cell is available to reach high pressure [1,13–15]. A clamp-type pressure cell is much more convenient and available to various methods in which a larger sample volume is needed. However, the usual clamp-type pressure cell is made of CuBe alloy and the maximum pressure is 3 GPa at most. Hence, a microscopic study of the superconductivity has not been performed thus far although the superconductivity was discovered in 1996. Mayaffre *et al.* made NMR measurements under high pressure up to 3 GPa for the field (H) perpendicular to the plane, crystal b axis and suggested that the spin gap is suppressed by applying pressure [16,17]. However, the measurements were in fact done not in the superconducting state but in the normal state above T_c.

In the present work, we have used a clamp-type pressure cell made of NiCrAl alloy and performed NMR measurement at pressures more than 3 GPa by applying the field parallel to the leg direction, crystal c axis. This enabled us to study the superconducting state on a microscopic level for the first time and to investigate pairing symmetry as well as the relation between the spin gap and the superconductivity.

A single crystal of $Sr_2Ca_{12}Cu_{24}O_{41}$ with a volume of 4 mm × 2 mm × 1 mm was prepared for the measurements. The clamp-type pressure cell with an effective sample space of $\phi 4 \times 20$ mm was used for the measurement. The appearance of the superconductivity was confirmed by measuring resonance frequency of a NMR probe attached to the pressure cell. The resonance

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frequency is roughly given as $f \propto 1/\sqrt{LC}$, where L and C represent inductance and variable capacitance of the NMR probe, respectively. The sample is contained in a coil and the onset of superconductivity is detected by the change of the resonant frequency, i.e., the change of L value. This method corresponds to ac susceptibility measurement. The T dependence of the frequency at several fields is shown in Fig. 1. If we probe the temperature at which the resonance frequency starts to change against H, this gives H_{c2} vs T_c characteristics as is shown in the inset. For high-T_c cuprates, the temperature has been identified as irreversibility temperature T_{irr} [18]. T_{irr} gives a borderline between creeping and freezing of flux lines (FL) which are formed through the planes for the H perpendicular to the plane. In the present case, flux lines are self-trapped between the planes since the field is applied parallel to the plane, and thus such a creep is hardly expected.

^{63}Cu-NMR signals for the ladder site can be separated from those for the chain site since nuclei of these sites possess different quadrupole coupling [8,19]. We have reported NMR spectra under pressure measured by using the present crystal in Ref. [20]. The NMR spectra at 3.5 GPa were almost the same with those at ambient pressure. One signal corresponding to the central transition ($I = -1/2 \Leftrightarrow 1/2$) of ^{63}Cu nuclei was observed for the ladder site and the relaxation rate (T_1^{-1}) was measured at 70.0 MHz which corresponds to 6.2 T. T_c at this field is about 2.8 K as is seen from the inset of Fig. 1. The T dependence of T_1^{-1} is shown in Fig. 2. The spin gap is observed even under high pressure as an activated T dependence of T_1^{-1} at temperatures higher than 30 K, i.e.,

$$T_1^{-1} \propto \exp(-\Delta_{\mathrm{spin}}/T). \quad (1)$$

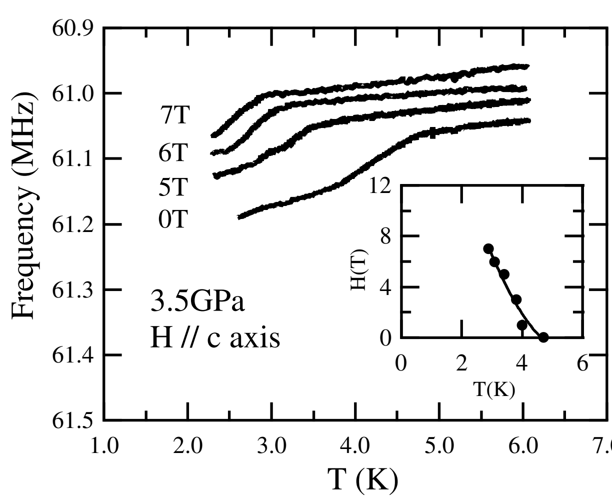

FIG. 1. Resonance frequency of a NMR probe attached to a pressure cell. The frequency changes at the superconducting state. The onset corresponds to the upper critical field. The inset shows the H_c-T_c curve obtained from the onset of the frequency at each field. The solid line is a guide for the eyes.

The value of Δ_{spin} is estimated to be 173 K. It should be noted that the spin gap is seen in the state in which the charge transport is metallic [13].

By contrast, T_1^{-1} below 30 K is dominated by a term showing T-linear dependence followed by a peak developed below T_c. The onset and the position of the peak shift to higher temperature with decreasing the magnetic field to 5.0 T (open squares in Fig. 2). If the T-linear component originates from extrinsic source, it should be persistent in the superconducting state. However, T_1^{-1} measured at low temperatures obviously goes below the T-linear line shown in the figure. Then, such a case is excluded. As for the peak, the possibility of vortex motion might be pointed out. The vortex motion has been observed from T_1^{-1} of ligand sites in high-T_c cuprates such as $YBa_2Cu_4O_8$ (YBCO) [21] or $HgBa_2CuO_{4+\delta}$ (HBCO) [22] when the H is applied perpendicular to the plane. The FL is self-trapped between the planes for the H parallel to the plane, and thus the effect is hardly expected in the present case. In fact, the effect disappears when the H is applied parallel to the planes in the HBCO system [22]. Furthermore, T_1^{-1}/γ_N^2 (γ_N: nuclear gyromagnetic ratio) at the peak is 80 or 25 times larger than those for YBCO or HBCO, respectively. The value is too large to explain the peak due to vortex motion. Hence, we conclude that the peak of T_1^{-1} and the T-linear component have the same origin in the electric state and/or spin fluctuations. The peak can be assigned to a superconducting coherence peak and the T-linear dependence of T_1^{-1} to Korringa-type behavior,

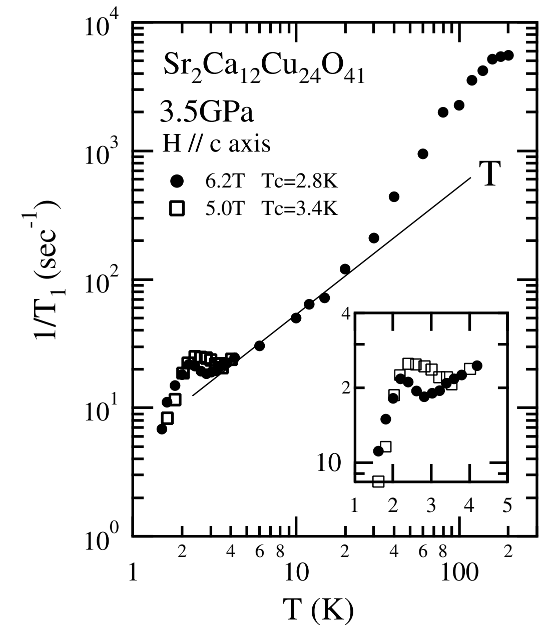

FIG. 2. Nuclear magnetic relaxation rate $1/T_1$ for ^{63}Cu nuclei. A solid line shows Korringa relation expressed by Eq. (2). $1/T_1$ at low temperatures around T_c is expanded in the inset.

$$T_1^{-1} \propto bT, \qquad (2)$$

where the value of b is about 6.1 ($\mathrm{sec}^{-1}\,\mathrm{K}^{-1}$). The observation of the clear peak implies that a finite gap exists in the quasiparticle excitation at all wave vectors. In the meaning that there exist no nodes in the pairing symmetry, the superconductivity possesses an *s*-wave-like character.

The spin gap is also observed in ^{63}Cu-NMR shift (K) at relevant temperatures. The shift shows H^{-2}-linear dependence because a large quadrupole effect acts on ^{63}Cu nuclei. The values free from the quadrupole effect are obtained by plotting K vs H^{-2} and extrapolating to zero field [23]. The values at high temperatures are shown in Fig. 3. The shift is given as a sum of two components, the orbital and the spin parts ($K = K_{\mathrm{orb}} + K_{\mathrm{spin}}$), and the spin part is proportional to the spin susceptibility. The T dependence of K at high temperatures fits well the theoretical curve for a spin-ladder system [24],

$$K(T) = K_0 + \frac{K_1}{\sqrt{T}} \exp(-\Delta_{\mathrm{spin}}/T). \qquad (3)$$

The gap Δ_{spin} obtained from the fit is 217 K and is comparable with that estimated from T_1^{-1}. The value of K_0 is estimated to be 0.25%. The main contribution of K_0 comes from K_{orb} comparable with that for high-T_c cuprates (K_0 of YBCO, for example, is 0.28% [25]). The paramagnetic contribution corresponding to the Korringa term in T_1^{-1} [Eq. (2)] should be included in K_0.

The shift in the low temperature region around T_c is shown in Fig. 4. The raw data at several fields are also plotted in the figure since T_c depends on the fields. As seen from the figure, no appreciable change is seen at T_c. The paramagnetic contribution in K_0 should be considerably small so that a change at T_c might be difficult to detect within the present experimental accuracy.

We have observed from T_1^{-1} and K unexpected features in both normal and superconducting states. At a pressure of 3.5 GP, we observed two excitation modes in the normal metallic state; one gives rise to the gapless T-linear component in T_1^{-1} ($T_1^{-1} \propto bT$) which links directly with the superconductivity, and the other the activation-type component expressed in Eq. (1). The persistence of the spin gap at high pressures suggests that quasi-one-dimensional spin-charge dynamics is preserved in the normal state although pressure increases coupling or hopping between the ladders. In the case of conventional metals, the gapless T-linear component arises from paramagnetic free electrons; however, such a term is hardly expected in the present system unless peculiarity of the ladder structure is regarded, because the majority of spins falls into the spin-singlet state due to the existence of the large spin-gap Δ_{spin} at low temperatures.

Since the system is metallic under high pressure, the system should be treated in k space. However, microscopic snapshot in real space saves to understand the existence of the T-linear component as well as the activation-type component. The snapshot in real space can be described as follows: The ground state of the undoped ladders is understood as overlap of spin dimmers on the rung [4]. Hole doping implies breaking of spin dimmers on the rung and gives rise to the holon-spinon bound state [26]. At high temperatures singlet-triplet spin excitation in the spin dimmers away from the bound state dominates, which causes the activated behavior of $1/T_1$ as is illustrated in Figs. 5(A). At intermediate temperatures, the majority of the spin dimmers falls into the singlet ground state, but the spin in the bound states moves rather freely and contributes to the gapless T-linear component in T_1^{-1} [Figs. 5(B)]. The superconductivity would be realized by the pairing of two bound states as illustrated in

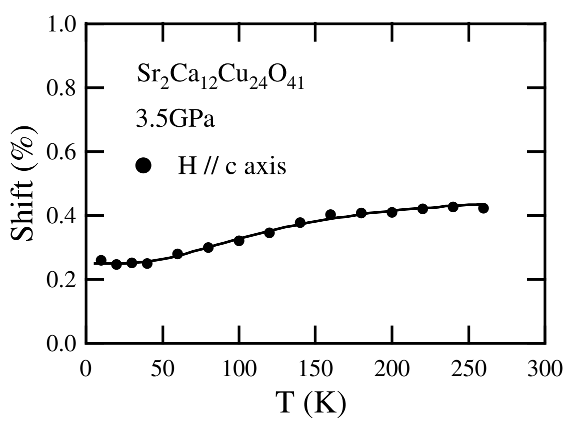

FIG. 3. NMR shift of ^{63}Cu nuclei for the ladder sites at high temperatures. The solid curve represents values calculated by Eq. (3) in the text.

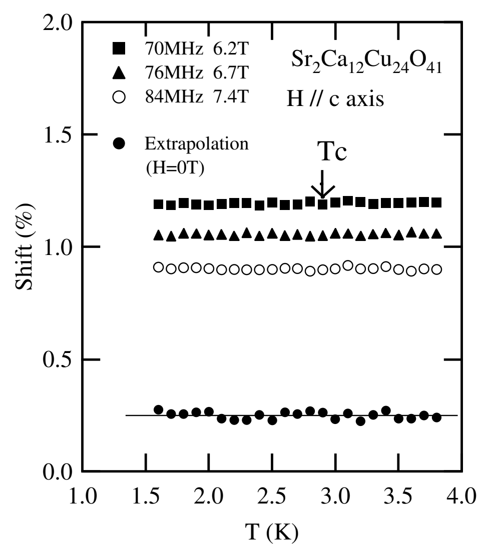

FIG. 4. NMR shift of ^{63}Cu nuclei for the ladder sites at low temperatures around T_c. The raw data which show the H^{-2}-linear dependence due to the quadrupole effect are also plotted in the figure.

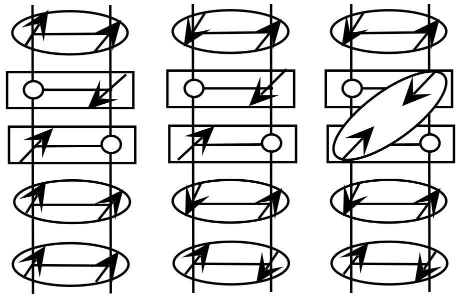

FIG. 5. (A) Illustration of spin and charge configuration at high temperatures. Ellipses show spin dimmers on the rung. Some of them are in the triplet states at high temperatures. A rectangle implies the holon-spinon bound states. They move independently in the ladder. (B) Illustration at intermediate temperatures. A spin within the holon-spinon bound state is free and paramagnetic. Spin dimmers in the ellipses are in the singlet state at this temperature region. (C) Illustration at the superconducting state. Two spins within the bound state form the pairing.

Figs. 5(C). In this viewpoint, the spin-gap formation observed from T_1^{-1} at high temperatures does not contribute to the pairing formation of the superconductivity.

Finally, it should be noted that the normal state in the present system is free from large antiferromagnetic fluctuation unlike high-T_c cuprates. T_1^{-1} in typical high-T_c cuprates such as YBCO systems is expressed as $a + bT$ above T_c where the T-independent term a represents the antiferromagnetic fluctuation [$a \sim 3 \times 10^3$ (sec^{-1}) and $b \sim 6$ ($\mathrm{sec}^{-1}\,\mathrm{K}^{-1}$) for YBCO] [27]. The antiferromagnetic fluctuation is extremely suppressed due to the existence of the spin gap in the present system, which might explain why high T_c is not realized in this system although the structure is quite similar to high-T_c cuprates.

In conclusion, we have succeeded in obtaining microscopic information of the superconducting state in $Sr_2Ca_{12}Cu_{24}O_{41}$ by applying pressure up to 3.5 GPa. In this material, we observed two excitation modes in the normal state. One gives rises to the activation-type component in T_1^{-1}, the other T-linear component linking directly with the superconductivity. The superconductivity possesses an s-wave-like character in the meaning that a finite gap exists in the quasiparticle excitation.

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