Nuclear Spin Relaxation in Hole Doped Two-Leg Ladders

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The nuclear spin-lattice relaxation rate $(1/T_1)$ has been measured in the single crystals of hole doped two-leg ladder compounds $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$ and in the undoped parent material $\text{La}_{6}\text{Ca}_6\text{Cu}_{24}\text{O}_{41}$. Comparison of $1/T_1$ at the Cu and the two distinct oxygen sites revealed that the major spectral weight of low frequency spin fluctuations is located near $q \sim (\pi, \pi)$ for most of the temperature and doping ranges investigated. Remarkable difference in the temperature dependence of $1/T_1$ for the two oxygen sites in the heavily doped $x=12$ sample revealed reduction of singlet correlations between two legs in place of growing antiferromagnetic correlations along the leg direction with increasing temperature. Such behavior is most likely caused by the dissociation of bound hole pairs.

KEYWORDS: spin ladder, spin gap, hole doping, NMR

There has been considerable interest in the hole-doped two-leg spin ladders since superconductivity was predicted to occur in such systems. It has been well established that undoped two-leg spin ladders have a resonating valence bond ground state and a finite gap for spin excitations. How the spin and charge dynamics as well as the nature of the ground state evolve with hole-doping is an issue of current interest. Both analytic and numerical theories predict that doped holes would be bound in pairs with a finite spin gap, leading to $d$-wave superconductivity unless dominated by charge order (CDW) instability. This prediction stimulated many efforts to realize hole doping into two-leg ladders. Of these, the $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$ is the only hole-doped material with two-leg ladder structure so far known that shows superconductivity.

The structure of this compound consists of alternating stack of the CuO$_2$ one-dimensional chain layers with the Sr layers between them. The average valence of Cu is 2.25, i.e. 1/4 holes per Cu are distributed among the ladder and the chain layers. Holes in the chain layers are highly localized and do not contribute to charge transport. The hole density in the ladder layers ($P_L$) of the $x=0$ sample ($\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$) is estimated to be rather small ($P_L \sim 0.05$) from optical measurements. Substitution with Ca for Sr promotes transfer of holes from the chain layers to the ladder layers. Thus the electrical resistivity decreases with $x$ and superconductivity appears for $x \geq 11$ under high pressure above 3 GPa. By substituting Sr or Ca with La, total number of holes can be reduced. All Cu ions are divalent carrying spin $1/2$ in $\text{La}_6\text{Ca}_6\text{Cu}_{24}\text{O}_{41}$ (hereafter abbreviated as $\text{La}_6\text{Ca}_8$), which can be regarded as the undoped parent material.

Spin excitations in the ladder layers have been studied by neutron scattering and NMR. Neutron scattering experiments in undoped $\text{La}_6\text{Ca}_8$ have shown a finite gap $\Delta \approx 32$ meV for spin excitations at the wave vector $(\pi, \pi)$. The gap persists upon doping and its magnitude remains nearly independent of doping up to $x=12$. Measurements of the nuclear spin-lattice relaxation rate $(1/T_1)$ and the NMR frequency shift at the ladder Cu sites also show approximately activated temperature dependences, apparently indicating a finite spin gap. However, it has been puzzling that the activation energy decreases dramatically with increasing $P_L$ contrary to the neutron results. Recent results of Cu NMR for $x=12$ under high pressure indicate that the spin gap vanishes in the normal state of the superconducting materials. Thus it is still controversial whether the superconductivity emerges from preformed holes in the RVB spin singlet background as the theories originally predicted.

In this paper, we discuss low energy spin dynamics at ambient pressure based on the results of $1/T_1$ measurements in three single crystals, the undoped $\text{La}_6\text{Ca}_8$ and the hole-doped $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$ with $x=0$ and $x=12$. Since a two-leg spin ladder is a quasi one-dimensional system with short range antiferromagnetic correlations, low energy spin excitations should be located near $q_x=0$ or $\pi$ ($2k_F$) in the reciprocal space, where $q_x$ is the wave vector along the leg direction. Spin excitations are further specified by the symmetry with respect to the interchange of two legs. Symmetric (antisymmetric) excitations are associated with $q_y=0$ ($q_y=\pi$). Thus there are four important spots in the $q$-space that could contribute to the low energy spin fluctuations. All of them contribute to $1/T_1$ at the Cu sites. However, antiferromagnetic spin fluctuations along the leg direction with $q_x \sim \pi$ do not contribute to $1/T_1$ at the leg oxygen (O1) sites, neither do fluctuations with $q_y \sim \pi$ to $1/T_1$ at the rung oxygen (O2) sites. Therefore, measurements of $1/T_1$ at different sites allow us to distinguish low energy spin fluctuations at different wave vectors.
Our results indicate that the dominant weight of low frequency spin fluctuations is located near \((\pi, \pi)\) for most of the doping and temperature range investigated. This implies that the activation energy of \(1/T_1\) at the Cu sites is determined by the damping of excitations near \((\pi, \pi)\) and should not be identified as the spin gap. The discrepancy with the neutron results is thus resolved. The mechanism of damping, however, depends on doping and is closely correlated with the transport behavior.

The single crystals used in the NMR experiments were grown in oxygen atmosphere by the travelling solvent floating zone method. The crystals were then annealed in oxygen gas containing 45\% \(^{15}\)O for isotopic exchange. The temperature dependence of \(1/T_1\) at the Cu and O1 sites are shown in Fig. 1 (b) and (c), respectively. A general expression for \(1/T_1\) at \(k\)-th sites is given in terms of dynamic spin correlation function \(S(q, \omega_n)\) as

\[
(1/T_1)_k = 2\left(\frac{k \gamma}{\kappa}\right)^2 \sum_q \left(k F\beta(q)^2 + k F\gamma(q)^2\right) S(q, \omega_n).
\]

Here, \(\kappa\) is the direction of the external field, \(\beta\) and \(\gamma\) denote the directions perpendicular to \(\kappa\), \(k \gamma\) is the gyromagnetic ratio of the \(k\)-th nuclei, \(\omega_n\) is the nuclear resonance frequency (several tens of MHz), and \(k F\alpha(q)\) is the wave-vector dependent hyperfine coupling constant. The \(q\) dependence of \(F(q)\) describes the filtering of spin fluctuations in the \(q\)-space for each site mentioned before. The values of \(F\alpha(0)\) have been determined from the NMR frequency shift measurements up to an overall multiplicative factor. We define the normalized \(1/T_1\) by

\[
\frac{k W_\alpha}{C} \equiv \frac{(1/T_1)_k}{\left(\frac{k \gamma}{\kappa}\right)^2 \sum_q \left(k F\beta(q)^2 + k F\gamma(q)^2\right) S(q, \omega_n)}.
\]

where \(C = \left(\frac{1}{\kappa}\right)^2 \left(\frac{\kappa}{\gamma}\right)^2\left(\frac{\beta}{\gamma}\right)^2\left(\frac{\gamma}{\beta}\right)^2\) so that \(\frac{1}{\kappa} W_\alpha\) is identical to \((1/T_1)_k\). If there is no filtering, the value of \(\frac{1}{\kappa} W_\alpha\) should be identical for all nuclei. Experimentally, however, the values and temperature dependence of \(\frac{1}{\kappa} W_\alpha\) are quite different for the Cu and O1 sites, as one can clearly see by plotting the ratio \(\frac{1}{\kappa} W_\alpha\) shown in Fig. 1 (d).

1. Undoped La6Ca8: In the undoped La6Ca8, \(1/T_1\) shows an activated temperature dependence above 150 K with the activation energy of about 540 K at both sites. Below about 100 K, however, \(1/T_1\) shows a \(T\)-independent finite value. This is most likely due to the coupling to the magnetic CuO\(_2\) chain layers. It has been established that for one dimensional spin systems with a finite gap, spin correlation functions near zero frequency at low temperatures are described by the two magnon processes of thermally excited magnons with the momentum transfer \(q \sim (0,0)\). Then we expect the normalized \(1/T_1\) to be identical for all sites. However, \(Cu W_b/\gamma W_b\) shown in Fig. 1 (d) is much larger than one for the whole temperature range and increases with temperature above 150 K. This indicates that \(S(\pi, \pi) > S(0,0)\) and \(S(\pi, \pi)\) is more enhanced at higher temperatures. (For the rest of the paper, we omit \(\omega_n\) in \(S(q, \omega_n)\) so that \(S(q, \omega) = S(q, q, \omega = 0)\).)

The magnitude of \(S(\pi, \pi)\) is given by the \(\omega=0\) spectral weight of the magnon states broadened by lifetime (damping) effects due to multimagnon processes such as scattering of single magnons with two magnon continuum. It has the temperature dependence \(\exp(-2\Delta/T)\) in the low temperature limit and, therefore, should be negligible compared with \(S(0,0) \sim \exp(-\Delta/T)\). However, numerical studies have shown that the validity of such argument is limited to very low temperatures. Monte Carlo and DMRG calculations have shown that \((\pi, \pi)\) contribution becomes dominant even the temperature is as small as 0.3\(\Delta\) when the exchange along the leg is equal or larger than the exchange along the rung. Such anisotropy of the exchange constants is indeed suggested from analysis of the NMR frequency shift at the two oxygen sites.

Imai et al. found a crossover near 430 K in La6Ca8, above which \(1/T_1\) and \(1/T_2\) show remarkably different temperature dependences. They argued that...
two magnon processes with \( q \sim (0,0) \) is dominant below this temperature. However, the comparison of the magnitude of \( 1/N_{\text{Cu}^3}T_1 \) and \( 1/N_{\text{O}^{17}}T_1 \) in our data and closer examination of their temperature dependences indicate that \( q \sim (\pi,\pi) \) contribution becomes dominant already for \( T \gtrsim 150 \text{K} \).

2. **Lightly doped \( x=0 \):** The lightly doped \( x=0 \) sample shows semiconducting temperature dependence of resistivity although it is reasonably conducting along the leg direction (5m\( \Omega \)cm) at room temperature. Comparison of the \( 1/T_1 \) data for La6Ca8 and \( x = 0 \) in Figs. 1 (b) and (c) shows that slight hole-doping causes significant enhancement of \( 1/T_1 \) above 200 K, where holes become mobile and responsible for incoherent transport. This enhancement is much larger at the Cu sites than at the O1 sites.

Fitting of the \( 1/T_1 \) data above 200 K to an activated temperature dependence results in quite a large value of the activation energy (\( \sim 800 \text{ K} \)) at both sites, which is much larger than the spin-gap of 32.5 meV obtained from neutron scattering measurements at 20 K. The value of \( N_{\text{Cu}^3}W_{\text{b}^1}/N_{\text{O}^{17}}W_{\text{b}} \) for \( x = 0 \) is larger than that for La6Ca8 (Fig. 1 (d)), indicating that \( S(\pi,\pi) \) is further enhanced over \( S(0,0) \) by hole-doping. This result implies that incoherent motion of holes further accelerates the magnon damping, thereby increases the zero energy spectral weight near \( (\pi,\pi) \) and makes \( S(\pi,\pi) \) by far the most dominant contribution to \( 1/N_{\text{Cu}^3}T_1 \). The two oxygen sites show similar temperature dependence of \( 1/T_1 \), as shown in Fig. 1 (c).

Several anomalies of charge properties have been observed near 200 K for \( x = 0 \), supporting our argument relating the enhanced \( 1/T_1 \) above this temperature with motion of holes. At the Cu sites, \( 1/T_1 \) measured by zero field NQR is strongly enhanced below 180 K by quadrupolar relaxation due to slow fluctuations of electric field gradient. Analysis based on the standard motional narrowing theory indicates that glassy charge freezing occurs in this temperature range. The electrical resistivity plotted against \( 1/T \) also shows clear change of the activation energy from 1400 K for \( T \lesssim 180 \text{K} \) to 2200 K for \( T \gtrsim 180 \text{K} \). The values of electric field gradient at the Cu and two oxygen sites also show sudden steep increase above 200 K. These results indicate that both static charge distribution and charge dynamics change their behavior near 200 K.

3. **Heavily doped \( x = 12 \):** The data for \( x = 12 \) sample in Fig. 1 (b) and (c) indicate that further hole-doping up to \( P_L = 0.2 \) (\( x = 12 \)) significantly lower the temperature range in which \( 1/T_1 \) shows rapid variation. In order to compare \( 1/T_1 \) at various sites more clearly, we plotted the normalized relaxation rates \( N_{\text{Cu}^3}W_{\text{b}^1}/N_{\text{O}^{17}}W_{\text{b}} \) and \( N_{\text{O}^{17}}W_{\text{a}} \) in Fig. 2 (a). Their ratios are plotted in Fig. 2 (b).

Below about 60 K, \( N_{\text{Cu}^3}W_{\text{b}^1}/N_{\text{O}^{17}}W_{\text{b}} \) is relatively small (\( \sim 2 \)), indicating absence of strong enhancement of \( S(\pi,\pi) \) compared with other region in \( q \)-space. In the intermediate temperature range from 60 K to 180 K, where rapid increase of \( 1/N_{\text{Cu}^3}T_1 \) is observed, \( N_{\text{Cu}^3}W_{\text{b}^1}/N_{\text{O}^{17}}W_{\text{b}} \) also increases steeply and shows a broad maximum near 180 K. This means that \( S(\pi,\pi) \) is getting dominant over other components. Therefore, the variation of \( 1/N_{\text{Cu}^3}T_1 \) in this temperature range with an apparent small activation energy (\( \sim 200 \text{ K} \)) is not associated with thermal excitations across the gap but caused by accumulation of low frequency spectral weight near \( (\pi,\pi) \). Thus it is not in conflict with the neutron results that shows a large spin gap of 370 K in the low temperature limit (\( T = 7 \text{K} \)).

A remarkable feature for the heavily doped material is that the two oxygen sites show quite different temperature dependences of \( 1/T_1 \). Below 60 K, the ratio \( N_{\text{O}^{17}}W_{\text{a}}/N_{\text{O}^{17}}W_{\text{b}} \) is large (\( \sim 5 \)), indicating that \( S(0,\pi) \gtrsim S(\pi,0), S(0,0) \). As the temperature increases \( N_{\text{O}^{17}}W_{\text{a}}/N_{\text{O}^{17}}W_{\text{b}} \) falls rapidly and becomes smaller than one above 100 K, indicating that \( S(\pi,0) \gtrsim S(0,\pi), S(0,0) \). The temperature dependence of \( N_{\text{O}^{17}}W_{\text{b}}/N_{\text{O}^{17}}W_{\text{a}} \) combined with that of \( N_{\text{Cu}^3}W_{\text{b}^1}/N_{\text{O}^{17}}W_{\text{b}} \) suggests that singlet correlations along the rung becomes weaker with increasing temperature in place of the growing antiferromagnetic correlations along the leg. We should recall that such behavior has not been seen in \( x = 0 \) sample, where the two oxygen sites behave similarly up to room temperature. The spin susceptibility deduced from the shift measurements also shows rapid increase above 60 K and saturation above 180 K.

Above 180 K the behavior of \( 1/T_1 \) is quite different for all three sites. While \( 1/N_{\text{Cu}^3}T_1 \) shows gradual decrease after passing through a broad maximum around 180 K, \( 1/N_{\text{O}^{17}}T_1 \) and \( 1/N_{\text{O}^{17}}T_1 \) continue to increase. While \( 1/N_{\text{O}^{17}}T_1 \) varies almost linear in \( T \), \( 1/N_{\text{O}^{17}}T_1 \) increases more steeply, implying rapid enhancement of \( S(\pi,\pi) \). This is correlated with the continuous decrease of \( N_{\text{Cu}^3}W_{\text{b}^1}/N_{\text{O}^{17}}W_{\text{b}} \) to a modest value (\( \sim 4 \)), indicating that \( S(\pi,\pi) \) is getting comparable to \( S(\pi,\pi) \) at high temperatures. All these results suggest that the two legs of the ladder unit become gradually decoupled magnetically, hence no distinction between \( q_y = 0 \) and \( q_y = \pi \), and the spin gap near \( q_x \sim \pi \) is being filled with low frequency spin fluctuations. Indeed nearly constant \( 1/N_{\text{Cu}^3}T_1 \) and approximately \( T \)-linear \( 1/N_{\text{O}^{17}}T_1 \) are what would be expected for an isolated spin chains with gapless antiferromagnetic spin fluctuations. These results are consistent with the neutron scattering experiments for \( x = 11.5 \) by Katano et al. At \( T = 7 \text{K} \) the energy scan spectrum at \( (\pi,\pi) \) shows a peak at 32.5meV with no weight near \( \omega \sim 0 \). However, the spectrum at \( T = 200 \text{K} \) shows substantial weight be-
low 10 meV, even though the peak still appears at a high energy near 20 meV.

The temperature variation of the spin correlation discussed above is closely correlated with the transport behavior. Although the resistivity along the leg direction shows nearly $T$-linear metallic behavior down to 60 K, semiconducting behavior starts below 200 K along the rung direction. Motoyama et al. argued that such behavior is an evidence for the hole pairing as has been predicted theoretically. When holes are bound in pairs, coherent motion of hole pairs is possible only along the leg directions. Since the probability of interladder pair hopping is small, current along the rung direction has to be carried by quasiparticles that result from thermal dissociation of bound hole pairs. This picture is supported also by recent optical measurements.

Our results appear to be consistent with this argument. Starting from the low temperature side, dissociation of hole pairs begins to occur at about 60 K and almost completes near 180 K. Since hole pairing should be a necessary condition for the persistence of spin gap when doped with holes, dissociated quasiparticles carrying spin 1/2 will create spectral weight within the magnon gap. Moreover, such mobile quasiparticles will cause strong damping of magnons, filling the spin gap near $(\pi, \pi)$. It is also physically plausible that singlet correlations between the two legs is disturbed by motion of such quasiparticles, accounting for different behavior at the O1 and O2 sites. When hole pairs are completely unbound, the two legs will be highly decoupled and asymptotically behave as gapless Tomonaga-Luttinger liquid with strong antiferromagnetic correlation.

Numerical calculations for doped $t-J$ ladders have indeed demonstrated two distinct types of spin excitations at $T=0$. One is associated with the singlet-triplet excitations across the spin gap that evolve continuously from the magnon excitations in undoped material. The other is associated with the dissociation of bound hole pairs. Since the latter type has smaller excitation energy, it is reasonable that this process occurs at much lower temperatures than the spin gap in undoped material.

Magishi et al. argued based on their data of $1/CuT_1$ for $x=11.5$ that the opening of spin gap indicated by sudden decrease of $1/CuT_1$ below 180 K coincides with the onset of hole pairing inferred from the resistivity data. We should mention, however, that such crossover in $1/CuT_1$ is not limited to the heavily doped materials but common to wide range of doping. For example, Imai et al. observed similar crossover at 330 K (230 K) for $x=0$ ($x=3$), for which no evidence of hole pairing has been observed in transport or optical measurements. This indicates that for small doping, localization of individual holes rather than hole pairing is sufficient to restore spin gap behavior at low temperatures. We consider that the variation of singlet correlations along the rung is indicated by the temperature dependence of the ratio $O^1W_6/O^2W_4$ is the key factor related to the hole pairing and dissociation.

In conclusion, comparison of $1/T_1$ data at different sites indicates that the dominant weight of low frequency spin fluctuations is located near $(\pi, \pi)$ for most of the temperature and doping range we studied. The acti-