NMR Study of Carrier Doping Effects on Spin Gaps in the Spin Ladder $Sr_{14-x}A_xCu_{24}O_{41}$ ($A =$ Ca, Y, and La)

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Carrier doping effects on spin dynamics in $Sr_{14-x}A_xCu_{24}O_{41}$ ($A =$ Ca, Y, and La) are investigated by Cu NMR and NQR. The energy gaps in the spin excitation spectra (spin gap) are confirmed to be $\Delta = 140$ K for the CuO_2 chain and $\Delta = 470$ K for the Cu_2O_3 ladder in $Sr_{14}Cu_{24}O_{41}$. The spin gap for the ladder increases with the Y and La substitutions for Sr (up to $x = 3$), while it decreases with increasing x in $Sr_{14-x}Ca_xCu_{24}O_{41}$ and seems to collapse around $x = 13$ of the Ca substitution. Hole-doping effects on the spin gaps for the ladder configuration are interpreted in terms of magnon and hole-depairing excitations for the spin $S = \frac{1}{2}$ ladder. [S0031-9007(97)02578-7]

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The discovery of high-T_c superconductivity in lightly doped antiferromagnets has provided much interest in low-dimensional quantum spin systems. In order to obtain insight into the physics of the high-T_c superconductivity, the Heisenberg spin-ladder systems, which consist of two (or more) chains of magnetic coupled ions, have been investigated intensively, since novel quantum phenomena appear in spin-ladder system [1–6]. The spin degree of freedom in the single ladder is well described by the Heisenberg Hamiltonian

$$H = J\Sigma S_i S_{i+1} + J'\Sigma S_j S_j ,$$

where J and J' are exchange couplings along the legs and the rungs of the ladder, respectively. Recent theories predicted that the $S = \frac{1}{2}$ antiferromagnetic spin ladder forms a spin liquid state and has an energy gap in the spin excitation spectra (spin gap) for ladders with even numbers of leg, but has no gap for odd-numbered leg systems. Theories [3,4] predicted also that the frustrated spin liquid state with a spin gap translated into the superconducting state for hole doping.

The magnetic and electronic properties have been investigated in ladder systems of a vanadyl pryophosphate, $(VO)_2P_2O_7$ [7–9], and a cuprete $Sr_{n-1}Cu_{n+1}O_{2n}$ ($n = 3, 5, \ldots$) [10,11], though carrier doping into those systems has not been successfully achieved yet. Magnetic susceptibility [7,10], neutron scattering [8], and NMR studies [9,11] on those undoped ladder systems have provided a clear evidence for the formation of gaps for the low lying spin excitations. We have investigated Cu-NMR and Cu-nuclear quadrupole resonance (NQR) of a newly disclosed ladder system of $Sr_{14}Cu_{24}O_{41}$ [12,13] in which carriers are possibly controlled [14]. The $Sr_{14}Cu_{24}O_{41}$ system forms a unique structure with CuO_2, Cu_2O_3, and Sr layers. The CuO_2 layers consist of 1D chains of edge-sharing CuO_4 clusters and the Cu_2O_3 layers form 2D planes with two-leg ladder configurations [12,13]. Carriers in the Cu_2O_3 ladders and the CuO_2 chains are controlled by the substitution of other divalent (Ca^{2+}, Ba^{2+}) or trivalent (La^{3+}, Y^{3+}) elements for Sr^{2+} [15–17]. Very recently, superconductivity of $T_c \sim 10$ K was observed in the highly doped sample of the Ca substitution for Sr, when high pressure of $\sim$3 GPa was applied [18].

In a previous paper [19], we have confirmed the existence of the energy gaps in spin excitation spectra in both Cu sites by NMR/NQR measurements, as we have observed Cu-NMR/NQR signals of the chain and ladder site separately. We assign the gap energy of $\Delta = 140$ K for the CuO_2 chains and $\Delta = 470$ K for the Cu_2O_3 ladder in $Sr_{14}Cu_{24}O_{41}$. The value of 140 K is close to the 11 meV peak and $\Delta = 470$ K is close to the 35 meV peak for inelastic neutron experiments [20,21]. The difference in the spin gap between the chain and the ladder is attributed to the large exchange coupling in the ladder and the small one in the chain, which may be owing to the different atomic bond configurations; namely 180° Cu-O-Cu bond for the ladder and the nearly 90° Cu-O-Cu bond for the chain [12,13].

In this Letter, we report carrier doping effects on the spin gaps in both sites in $Sr_{14-x}A_xCu_{24}O_{41}$ ($A =$ Ca, Y, and La). The main results are as follows. The spin gap for the ladder increases with Y and La substitutions for Sr, decreases with increasing x in $Sr_{14-x}Ca_xCu_{24}O_{41}$, and seems to collapse around $x = 13$ of the Ca substitution. We will discuss hole-doping effects on the gap energy of spin excitation spectra in terms of magnon and hole-depairing excitations.

Polycrystalline samples were prepared by a conventional solid state reaction under ambient pressure [15–17]. NMR and NQR were measured by a conventional phase coherent pulse method. Two kinds of Cu-NQR signals were obtained separately around 30–34 MHz (Cu(1) chain signals] and 13–15 MHz [Cu(2) ladder signals] under zero applied field [19], corresponding to the two

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Cu sites of the chain and the ladder configurations in $Sr_{14}Cu_{24}O_4$. The split Cu-NMR spectrum of $Sr_{14}Cu_{24}O_{41}$ was analyzed well by taking into account the quadrupole interactions for both sites as reported previously [19].

From the edge position of the quadrupole split central transition (due to the second order perturbation effect) of Cu(1)-NMR, we evaluate the NMR shift K of Cu(1) in $Sr_{14}Cu_{24}O_{41}$ and show its temperature dependence in Fig. 1. K shows a maximum near 70 K and changes rapidly with decreasing temperature. The NMR shift consists of both orbital and spin parts $K = K_{\text{orb}} + K_{\text{spin}}$ for the transition metal element. K_{orb} is considered to be temperature independent in general and is estimated to be in the range of $(+1 \sim +2)\%$ for Cu^{2+} [22]. Therefore, the observed positive K of $+1.74\%$ at $T \rightarrow 0$ can be reasonably attributed to K_{orb}, for the Cu^{2+} configuration, and the temperature-dependent part of K is attributed to K_{spin}. As shown in the inset of Fig. 1, the temperature dependence of K_{spin} of Cu(1) obeys a linear relation of magnetic susceptibility χ_{corr} (after subtracting the Curie-Weiss type contribution from impurity- or isolated-Cu^{2+} spins [15]) with an implicit parameter of temperature. Below 100 K, only the susceptibility from the chain site is dominant as the contribution from the ladder is considered to be negligible due to the large energy gap as discussed below. Thus, the transferred hyperfine constant $H_{\text{hf}}^{\text{spin}}$ for Cu(1) is obtained to be -82 kOe/μ_B from the relation of $H_{\text{hf}}^{\text{spin}} = N_A \mu_B K(T)/\chi_{\text{corr}}$.

We measured T_1 of Cu(1)-NQR (at 33 MHz) and Cu(2)-NMR in $Sr_{14}Cu_{24}O_{41}$ by a conventional recovery method from a saturation pulse. Recovery of the nuclear magnetization after a saturation pulse for Cu(1)-NQR and Cu(2)-NMR spectra does not follow a recovery relation expected for a unique T_1 process. Instead, the recovery $R(t)$ of spin echo intensity in both Cu sites was well fitted to the relation of $R(t) = \{[M(\infty) - M(t)]/M(\infty)\} \exp[-(t/T_1)^n]$ with $n = \frac{1}{2}$, indicating the Gaussian-like distribution of the T_1 process. Figure 2 shows the temperature dependence of $1/T_1$ of Cu(1)-NQR at 33 MHz in $Sr_{14-x}A_xCu_{24}O_{41}$ ($A =$ Ca, Y, and La). $1/T_1$ decreases rapidly with decreasing temperature, showing an activation type behavior above 20 K. As the deviation at low temperatures is owing to additional contributions from impurity- or isolated-Cu^{2+} spins, we evaluate the gap value at high temperatures above 20 K and obtain the activation gap of $\Delta = 140$ K for the chain site. As can be seen in Fig. 2, the temperature dependence of $1/T_1$ of the Cu(1) site is similar for Ca, Y, and La substitutions.

As shown in Fig. 3, the temperature dependence of $1/T_1$ of the Cu(2) site obtained from the central peak in the NMR spectrum also shows an activation type behavior at high temperatures, except below 50 K where T_1 tends to be constant. The gap of $\Delta = 470$ K for the Cu(2) ladder site is obtained from the simple relation of $1/T_1 \propto \exp(-\Delta/T)$ for $Sr_{14}Cu_{24}O_{41}$ [23]. For the Ca-substitution case, $1/T_1$ becomes smaller with decreasing temperature compared to the case of $Sr_{14}Cu_{24}O_{41}$, indicating the gap

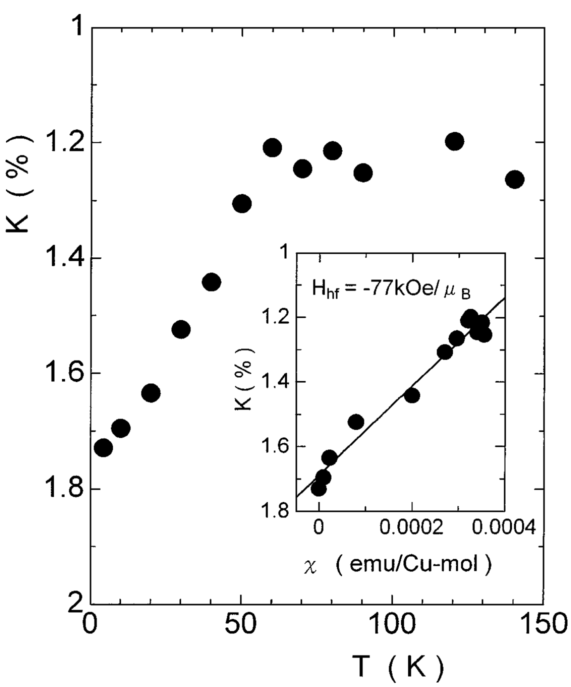

FIG. 1. Temperature dependence of NMR shift K of Cu(1)-NMR spectrum of $Sr_{14}Cu_{24}O_{41}$. Note that K is shown by the negative direction. The inset shows Knight shift K vs magnetic susceptibility χ^{17} as a function of temperature as an implicit parameter.

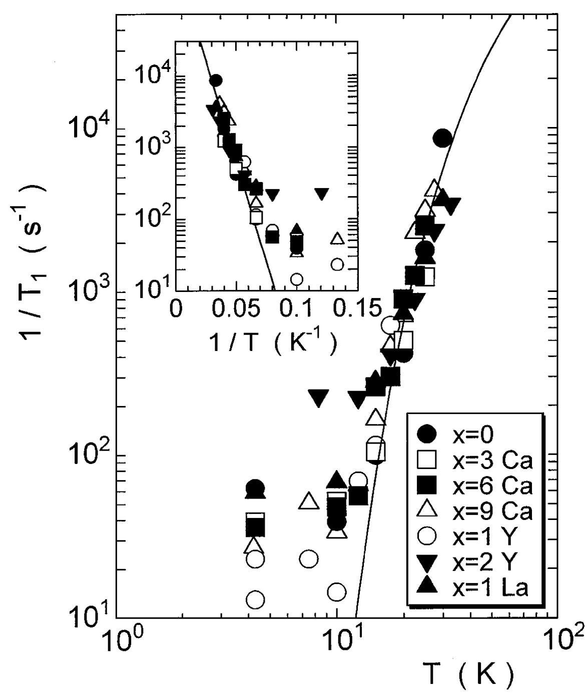

FIG. 2. Temperature and inverted-temperature dependence of $1/T_1$ of ^{63}Cu(1)-NQR in $Sr_{14-x}A_xCu_{24}O_{41}$ ($A =$ Ca, Y, and La). The solid lines correspond to the $\exp(-\Delta/T)$ relation with a gap of 140 K.

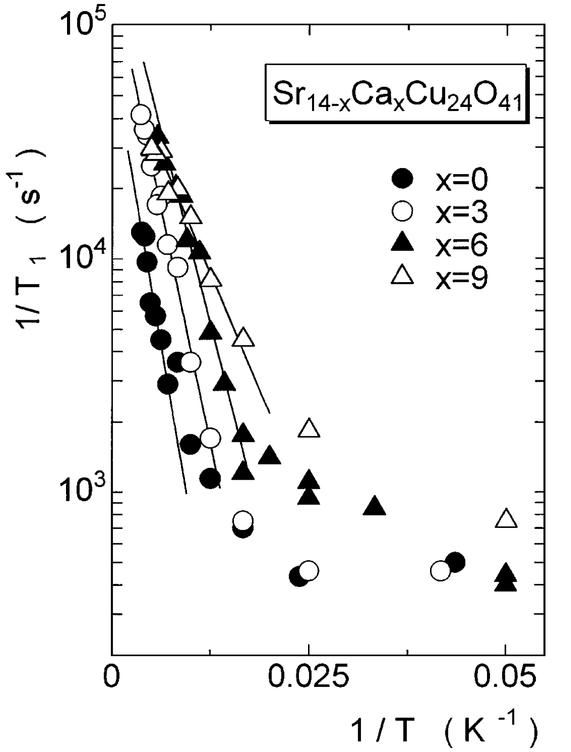

FIG. 3. Inverted-temperature dependence of $1/T_1$ of ^{63}Cu(2)-NMR in $Sr_{14-x}Ca_xCu_{24}O_{41}$. The solid lines are obtained by least mean square fittings for exponential relations at the high temperature range.

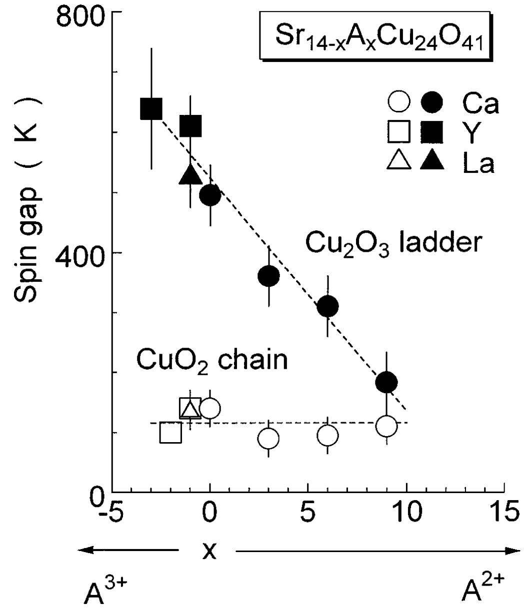

FIG. 4. x dependence of the spin gaps for the ladder site (●, ■, ▲) and the chain site (○, □, △) in $Sr_{14-x}A_xCu_{24}O_{41}$ (A = Ca, Y, and La).

energy decreases with x of Ca. Figure 4 shows the x dependences of gap energy for both Cu sites obtained from the temperature dependence of $1/T_1$. We would like to stress that the spin gaps of the Cu(1) chain site up to $x = 9$ of Ca, up to $x = 2$ of Y, and up to $x = 1$ of La are nearly identical to (or a little smaller than) that of nondoped $Sr_{14}Cu_{24}O_{41}$. However, the spin gap of the Cu(2) ladder site increases with x of Y and La, and decreases with x of Ca. From the linear extrapolation with x, the spin gap for the ladder site seems to disappear at around $x = 13$ in $Sr_{14-x}Ca_xCu_{24}O_{41}$. This finding suggests that the spin gap for the ladder site collapses with hole doping at a sufficient level where the ladder system is expected to be metallic [15] and superconducting [18].

First, we discuss the spin gap for the chain site. According to the electrical resistivity measurement, $Sr_{14}Cu_{24}O_{41}$ is semiconductive in spite of an average valence of Cu ions of +2.25. This system becomes more insulating with increasing x for A = Ba, Y, and La, while it becomes more conductive for A = Ca, [15–17]. The bond-valence-sums calculation [16] has shown that most holes are localized dominantly in the CuO_2 chains and do not enter the Cu_2O_3 ladder planes for the nondoped $Sr_{14}Cu_{24}O_{41}$. In fact, the average valency of the chain Cu ions is estimated to be 2.55 by an iodometry titration and to be 2.53 from the analysis of magnetic susceptibility [17], values that are close to 2.60 expected when all holes are located in the chain of Cu ions. Thus, most holes are considered to be situated in the chain site and to be localized.

The number of Cu^{2+} $S = \frac{1}{2}$ spins in the chain is ~40% of the Cu ions of the chain in $Sr_{14}Cu_{24}O_{41}$. As two neighboring Cu^{2+} spins in the 1D chains couple antiferromagnetically to form a singlet, most of Cu^{2+} $S = \frac{1}{2}$ spins (40% of the Cu ions) among the comparable amount of Cu^{3+} ($S = 0$) ions may form dimers, a finding that has been supported by the recent neutron scattering experiment [21]. For the 1D chain spins with alternating interactions (dimerized spins), theory has shown the existence of the gap for magnon excitation spectra [24]. This may be an interpretation for the origin of the spin gap for the CuO_2 chains in $Sr_{14}Cu_{24}O_{41}$. The relatively small gap of 140 K is attributed to the small exchange interaction owing to the edge-sharing CuO_4 bond for the chain configuration in $Sr_{14}Cu_{24}O_{41}$. As the NMR result shows the spin gap for the chain persists without notable change in the range of x for the Ca, Y, and La substitution for Sr, the AF exchange interaction between Cu^{2+} spins of the dimerized singlet pairs is not affected by increase or decrease in the number of singlet spin pairs in the chains under randomly distributed and localized holes.

Next, we discuss the change of spin gap in the ladders. Additional doping of holes induces the oxidation state and introduces effective Cu^{3+} ($S = 0$) ions in either chain or ladder sites. Kato *et al.* [15] suggest that the hole transfer from the CuO_2 chain to the Cu_2O_3 ladder planes occurs by the Ca substitution due to the shortening of the lattice constants. The hole transfer from the chain to the ladder sites is supported also by the bond-valence-sums calculation [16]. As a result, hole carriers situated in the ladder planes may participate in conducting without localization, when sufficient holes are doped. For the Y^{3+} and La^{3+} substitution, holes in the ladder as well as in the chains decrease owing to the difference of the charged state of Ca^{2+}.

As pointed out theoretically [6], the ground state of the ladder is a spin liquid state with a gap Δ for the isotropic ($J'/J = 1$) and also the strong ($J'/J > 1$) coupling. The excited sate in the doped ladder can involve spin-triplet rungs, similar to the nondoped ladder case. In addition, hole doping in the ladder creates the single-hole rungs or two-hole rungs. In the ground state for two holes, holes enter the bound state of two holes in the same rungs [6]. Therefore, in the doped ladder, there exist two different types of magnetic excitations, i.e., the singlet-triplet (magnon) excitations and the excitations in which a pair of holes is scattered into two separated quasiparticles. The former one is inherited from the undoped spin ladder. The collective magnon excitations which evolve continuously from the nondoped limit can be influenced by the quasiparticle excitations, especially when quasiparticles start to move along the legs. The mean field theory [3] shows an increase of the gap for the magnon excitations upon small doping, while numerical studies for the ladder indicate a decrease of the gap energy [6]. The discrepancy is considered to be due to the fact that the mean field theory predicted only the magnon excitation and did not involve the hole-depairing excitations [6].

Assuming the antiferromagnetic exchange coupling between Cu^{2+} spins of the singlet pairs along the rungs is not affected by the increase or decrease in the number of singlets in the ladder, similar to the case of the chains, the spin gap for singlet-triplet magnon excitations is expected to persist for light hole doping. The large decrease of the spin gap for the ladder suggests an important influence of the hole-depairing excitations on the gap energy. Low-lying excitations for the hole depairing cause the suppression of the gap. The NMR results show the spin gap seems to collapse around $x = 13$ of the Ca substitution, at which range holes can move (become metallic). Though the binding pairs of holes are considered to be favorable for the superconducting condensation, it should be noted that recently discovered superconductivity ($T_c = 10$ K) under high pressure [18] appears in the doped range where the spin gap seems to disappear in the ladder. Needless to say, to confirm conclusively the important point whether or not the spin gap and the hole-pairing state for the Cu_2O_3 ladder persists in the superconducting state, we need to investigate NMR and neutron scattering experiments for the highly doped ladder samples under high pressure.

In summary, the spin gap of the order of 140 K for the chain is nearly independent of the substitution of Ca (up to $x = 9$), Y (up to $x = 2$), and La (up to $x = 1$) for Sr, but the spin gap for the ladder decreases with x and seems to disappear around $x = 13$ of the Ca substitution for Sr in $Sr_{14-x}A_xCu_{24}O_{41}$. The decrease of the spin gap energy upon hole doping in the ladder can be attributed to the evolution of spin excitations, which is owing to the increase of the excitations from bound holes into separated quasiparticles in the ladder planes.

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